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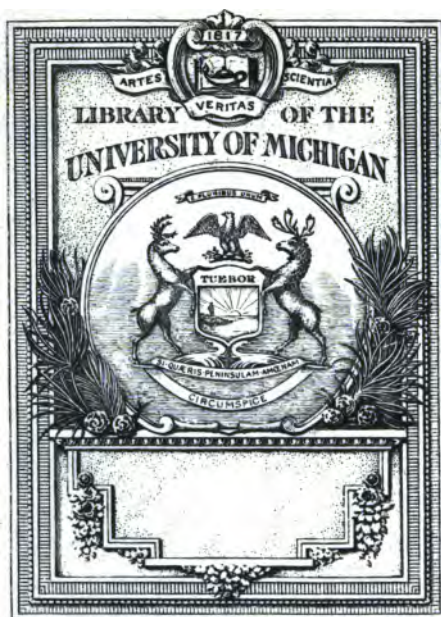
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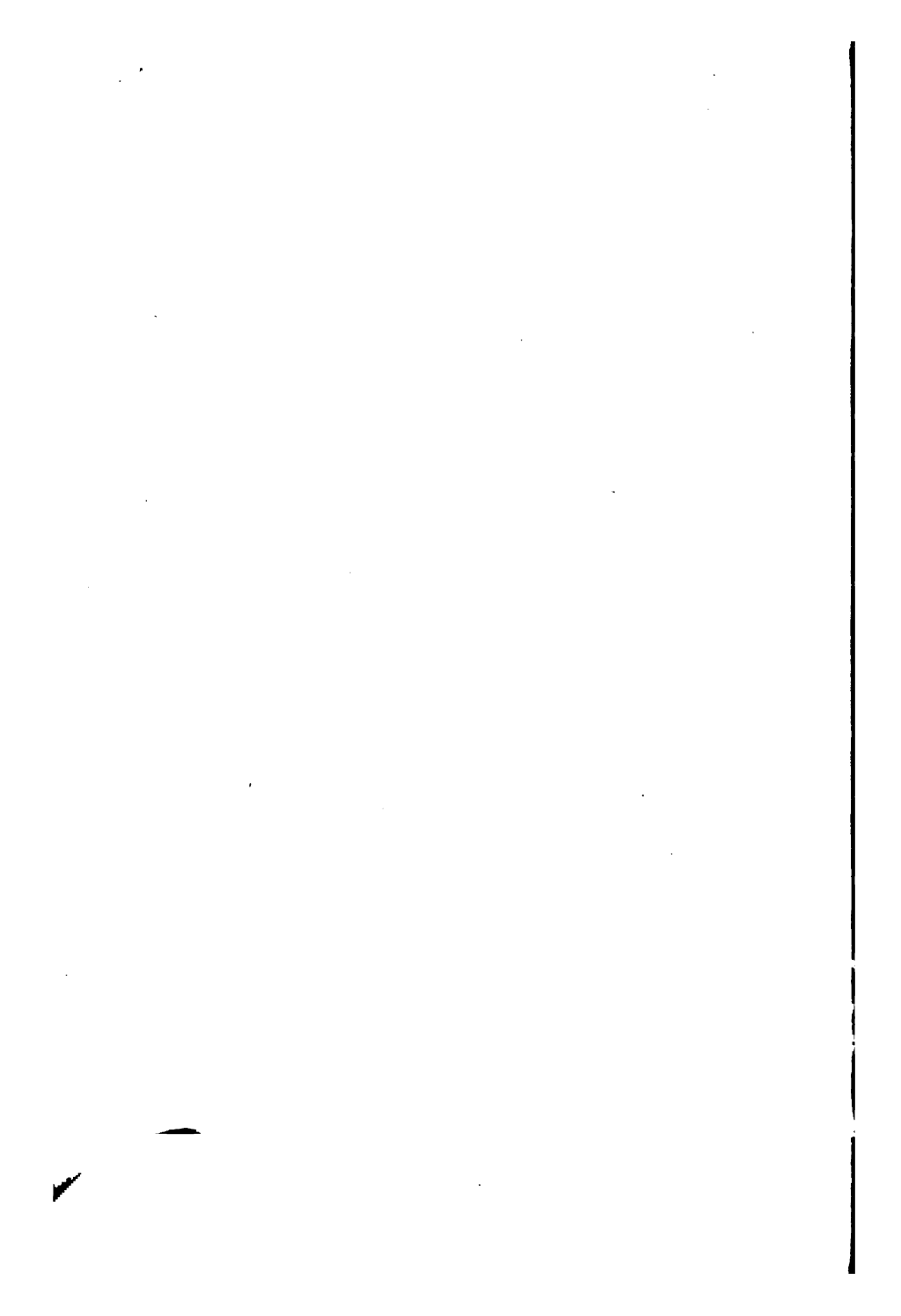


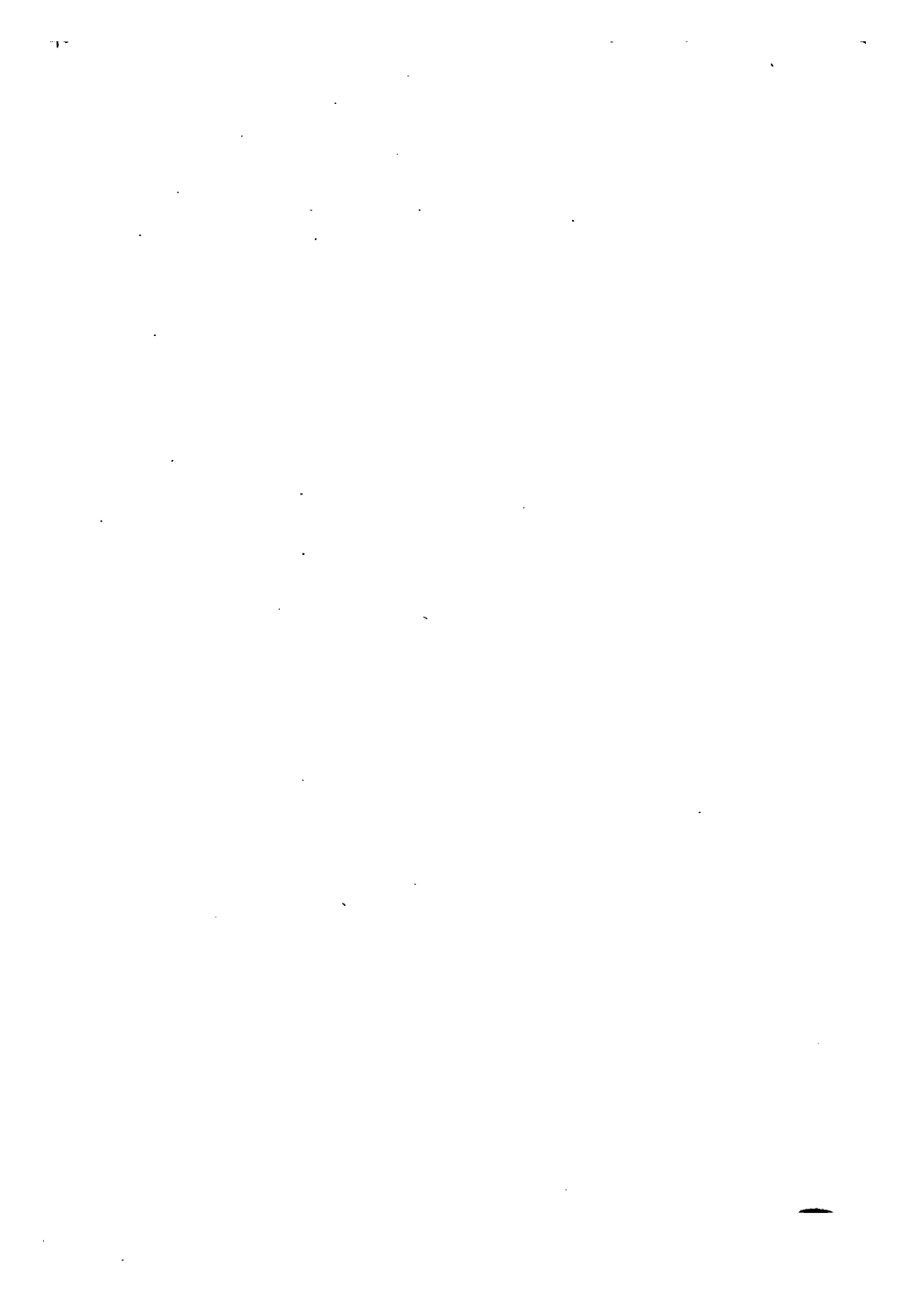
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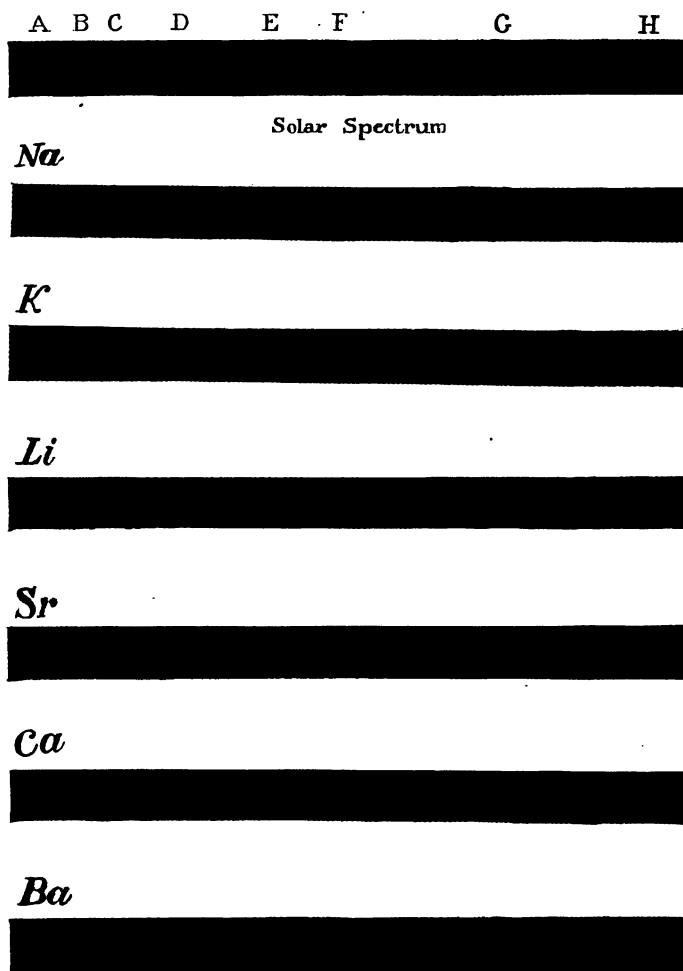


Fig. 33. Various spectra.
See page 107.

FIRST PRINCIPLES
OF
C H E M I S T R Y

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PREFACE

IN the early spring of 1904, the authors were appointed a joint committee of two organizations of New York science teachers, to prepare a syllabus for a first course in Chemistry. The fruit of their labor during the succeeding year was adopted in substance by the Department of Education as the syllabus for New York State. In planning this outline, the guiding principles were to make the experimental evidence precede the chemical theory, to follow as far as feasible the historical order in the development of the theory, and to emphasize the practical aspects of the science.

As there was no existing text-book written from the point of view contemplated by the syllabus, the preparation of the present book was begun in September, 1905. During the writing of the book, the authors have been constantly in close touch with one another, and the book is in every part the joint product of their efforts.

In selecting their material, the authors have been governed wholly by what they considered of intrinsic value to the elementary student, without reference to its traditional place in a text-book. This has led to the omission of some subjects commonly found in books for beginners. To the subjects selected they have striven to give a discussion simple enough to be readily comprehended by the beginner, and complete enough to furnish him with a clear idea of the underlying principles of Chemistry and a definite knowledge of its more important facts.

To this end, the experimental determination of chemical facts is emphasized from the first. When sufficient facts have been given to make explanation necessary, the generalizations

of the science have been introduced. In some of the theoretical chapters, particularly those on solution and ionization, it may be advisable to omit certain portions at first and to take them up afterwards as need arises. The authors have attempted to bring out the fundamental principles first by a simple statement, which is later developed and driven home by illustrations, exercises, and problems, all designed to stimulate the pupil to think for himself, and constantly to connect his new facts with the facts and principles already learned.

In order to give the pupil some idea of the great commercial importance of Chemistry, a number of typical manufacturing processes have been described and illustrated. Where a substance is manufactured in several ways, the authors have endeavored to avoid confusion by giving a description of one process only, selecting the one which they believe is, or will become, most extensively used in this country. For example, the time-honored chamber process for the manufacture of sulphuric acid has been omitted, because it is giving way to the contact process. The commercial production of copper, aluminum, iron, and carborundum have been described somewhat in detail, as they are notable examples of modern chemical processes.

The thanks of the authors are very gratefully given to all those who have so generously assisted them in securing descriptions and illustrations of chemical processes as they are actually carried on. Mr. Allen B. Doggett has rendered great assistance in photographic work. We are especially indebted to Mr. C. D. McArthur, for the drawing and description of the lampblack process; to our students, for the execution of many of the line drawings; to the Carborundum Company, the American Smelting and Refining Company, the National Lead Company, and to the *Scientific American*, for assistance which they have rendered.

NEW YORK, August, 1907.

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find any resemblance between iron and rust or between wood and what remains after it is burned. The iron and the wood have apparently disappeared or changed and we have a new substance in their places. Such alterations are called *chemical changes*. Chemistry is the name given to the science which has grown out of the study of chemical changes and the effort to control or modify them.

The most striking chemical change that goes on about us is that which occurs when a substance burns. If the burning substance is coal or wood, it seems to disappear except for a small quantity of ashes. In studying this change, several questions suggest themselves. What has happened to produce the heat that is given off? What has become of the great mass of substance that has apparently disappeared? Why does the substance burn more brightly when the air is blown on it? Why does it stop burning when the air is shut off, as in smothering the flame? If we find answers to these questions, we shall have explained the phenomena of burning.

Early investigators did not discover the true nature of this process. They adopted a wrong explanation, and, as a result, chemistry, as a science, did not advance. A true explanation was stated only a little more than a hundred years ago. Since that time chemistry has progressed at an astonishing rate. The true explanation of burning was found by studying the change that many metals undergo when heated in air.

3. Heating Metals in Air. — A few metals — for example, magnesium — burn when heated in the air. Most metals undergo a similar, but much slower, change, without the production of light. If a piece of bright copper is heated, it assumes a black color; on bending or scraping it gently

a black powder separates from it. If the metal is heated again, another layer of the black substance forms. By repeating the process a sufficient number of times, the piece of copper can be entirely changed into the black powder. Since the black powder in no way resembles the copper from which it was prepared, a chemical change has taken place. Iron heated in a similar manner gives a somewhat similar result. Lead after melting gives a yellowish powder; zinc, if in the form of a powder, will take fire and give a white powder. Metals, in general, when thus heated give powdered substances which bear no resemblance to the original metal.

Several things may be thought of as explanations of the change which these metals undergo. It may be that by the effect of the heat, without the aid of any substance, the metal is transformed into a new kind of matter; possibly the metal in being heated has lost some of its substance, which has passed off as gas; possibly the metal has absorbed something from the air.

As an aid in testing these possible explanations, it will be advisable to weigh the metal before and after it is heated. When this is done, it will be found that *the powder always weighs more than the metal* from which it was formed. This seems to indicate that during the heating the metal adds to itself more substance and that this substance is taken from the air. To further test this conclusion, a piece of metal can be sealed in a glass tube from which the air has been exhausted; *heated under these conditions, the metal is not changed.*

4. Lavoisier's Experiment. — Another conclusive experiment is one that was performed by Lavoisier, the French chemist, to whom is given the credit of discovering the

nature of this kind of chemical change. He put some tin in a good-sized glass flask and sealed it so that the air could neither enter nor leave it. He then heated the flask carefully for several days. At the end of this time he noticed that a certain amount of white powder had been formed. He next ascertained that the flask with its contents had not changed in weight. He then opened the neck of the flask and noticed that air rushed in. On again weighing the flask he found that it had increased in weight, and that this increase was equal to the increase which the tin had undergone on being converted into the white powder. He explained these facts as follows: the tin on being heated combined with some of the air in the flask, producing the white powder. The flask as a whole did not increase in weight because no air entered the flask to take the place of that which had combined with the tin. When the flask was opened, the air entered, causing the increase in weight.

From these facts it appears probable that the powdered substances are more complex than the metals from which they are formed; that is, they contain the metal plus something which has been taken from the air. Lavoisier undertook to find out the nature of the substance which was taken from the air.

5. Heating Mercury in Air.—Mercury, heated in the air, undergoes a much less rapid change than the metals of which we have been speaking. By keeping it at a temperature near its boiling-point for several days, a small quantity of a red powder is gradually formed (Fig. 1). If a quantity of this powder is heated in a glass tube to a temperature somewhat higher than that at which it was formed, a colorless gas is given off. If a glowing splinter

is inserted into the tube, it bursts into flame and burns brilliantly. The gas cannot be ordinary air, for a splinter does not behave so in air. A considerable quantity of the

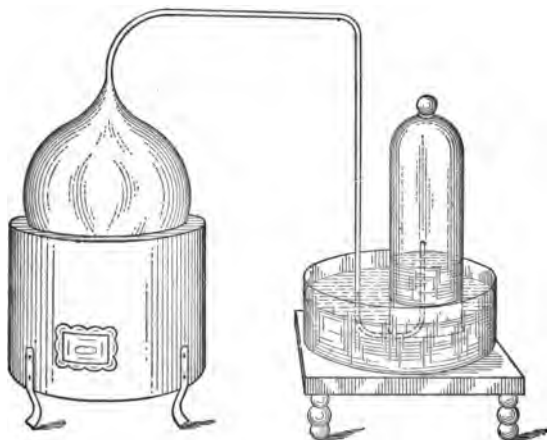


Fig. 1.

Lavoisier's apparatus for heating mercury.

gas can be collected and shown to be very different from ordinary air, in the fact that substances burn in it with extraordinary vigor.

On examining the tube it will be found that a part or all of the red powder has disappeared and that drops of mercury have collected on the sides of the tube. It appears from this experiment that *the red powder has decomposed into mercury and a gas* which readily supports combustion. Lavoisier named this gas *oxygen*.

Since the red powder was made by heating mercury in the air, and was not formed unless air was present, *the oxygen must have come from the air*. Hence air must contain oxygen. That air is not all oxygen is shown by the fact that only about one-fifth, and not all, of the air was

absorbed in Lavoisier's experiments; and also by the fact that substances do not burn as readily in air as in oxygen.

6. Burning. — The burning of wood or other substances is a process that closely resembles the change of a metal into a compound of the metal and oxygen. In the case of ordinary combustible materials, the products are chiefly gases which pass off unseen. By the use of suitable apparatus the products formed in the burning of a candle can be collected, and it is found that their weight is greater than the weight of the candle burned. As in the case of the metals, this increase in weight is due to the oxygen taken up from the air. If air is excluded, the burning substance is extinguished because it can no longer combine with oxygen. On account of the tendency of the substances to unite, energy is evolved in the form of heat.

7. Compounds and Elements. — We have shown that the red substance contains oxygen and mercury. The substance formed on heating copper in the air contains oxygen and copper. As these substances formed are composed of more than one kind of material, they are called *compounds*. No one has changed copper or mercury into anything else, without *adding something*. So far as we know, gold, iron, oxygen, and about eighty other things are not composed of anything else. They are simple, or, as we say, *elements*.

Summary.

Chemical changes involve change in the identity of the material. The composition of the substance is usually altered, and energy changes are also involved.

A compound is a substance that can be separated into two or more substances. An element is a substance which has not been separated into other substances.

When a substance burns in air, it combines with oxygen, forming a new compound.

Lavoisier obtained oxygen from air by heating mercury in it and then decomposing the material obtained.

Exercises.

1. Air and water were formerly called elements; why are they not now?
2. How could you prove that air contains oxygen?
3. What kind of change is involved in the withering of a leaf? making cloth from wool? baking bread? burning coal? extinguishing the coal?
4. Why is a candle extinguished by blowing?

CHAPTER II.

GASES AND THEIR MEASUREMENT.

8. Solids, Liquids, and Gases. — *Matter* is generally defined as anything that occupies space. The different kinds of matter are called *substances*. Substances differ in the way they fill space, and it is this difference that determines their *physical state*. The three physical states of matter are the solid, the liquid, and the gaseous.

A solid has a definite shape or *form*, and therefore a definite *volume*. A *liquid* has no definite form, but has, however, a definite *volume*. It can fill a vessel only to the extent of its volume and takes the shape of the containing vessel so far as it fills it. *Gases* have neither a definite form nor a definite volume. They tend to distribute themselves in all directions and fill completely any vessel into which they are brought. Their only boundaries are the containing walls.

9. Effect of Temperature and Pressure Changes on Volumes of Gases. — The measurement of the volume of gases usually involves a *correction of the gas volume*. This is necessary because the volume of a given quantity of gas is considerably affected by even slight changes in temperature and pressure. If the room gets warmer, the volume will be larger; if it gets colder, the volume will be less. Changes in atmospheric pressure will also cause the volume to vary. An increased pressure will mean a

diminished volume, and a decreased pressure an increased volume.

The measurement of gases in experiments like the analysis of air will be of little value for accurate work unless account is taken of the temperature and pressure changes. For this reason it becomes necessary to know to what extent these affect the volumes. This is not a difficult matter, for it is found that all gases contract or expand to almost exactly the same degree when they are subjected to the same changes. This regularity is somewhat surprising. A similar thing is not at all true for solids or liquids. Any observed regularity of this sort is called a *law*.

10. Charles' Law. — It is found that if a certain quantity of any gas is made to have a temperature of $0^{\circ}\text{C}.$, and then is warmed one degree, the gas expands $\frac{1}{273}$ of its volume. Warmed to 10° , it expands $\frac{10}{273}$ of its volume. Heated to 273° , its volume will be doubled. On cooling the gas, we find that it contracts $\frac{1}{273}$ of its

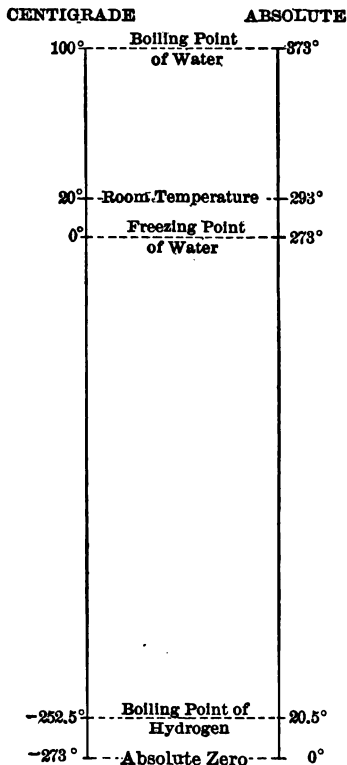


Fig. 2.
Centigrade and absolute
temperature scales.

volume at 0°C. for each degree. The general statement of these facts is known as Charles' Law. The best statement of it involves the use of the term *absolute temperature*.

By the absolute temperature is meant the temperature reckoned from the absolute zero, which is placed 273 degrees below the freezing-point of water (Fig. 2). The conception of the absolute zero has come from Charles' Law. A gas that followed this law perfectly would have zero volume at -273° . As a matter of fact, all known gases become liquids before this temperature is reached. Charles' Law may be stated thus:

The pressure remaining the same, the volume of a gas varies directly as the absolute temperature.

A Centigrade temperature is changed to an absolute temperature by adding it algebraically to 273 . Thus 24°C. becomes $297^{\circ}\text{ absolute}$ ($273 + 24$); -12°C. becomes $261^{\circ}\text{ absolute}$ ($273 - 12$).

11. Use of Charles' Law in correcting Gas Volumes. — By using this law we can calculate what will be the volume of a gas at a temperature differing from that under which it is measured. For example, a quantity of air measures 25.6 c.c. at a temperature of 21° . Find its volume at 0° .

$$21^{\circ}\text{C.} = 294^{\circ}\text{ abs.}$$

$$0^{\circ}\text{C.} = 273^{\circ}.$$

If the temperature of the gas were actually changed from 294° to 273° , it would be cooled, and would therefore contract. The volume at 273° will be less than the original volume. According to the law, it will be $\frac{273}{294}$ of its former volume. Hence:

$$\begin{aligned} x &= 25.6\text{ c.c.} \times \frac{273}{294} \\ &= 23.7\text{ c.c.} \end{aligned}$$

The temperature of 0° C. (= 273° abs.) is chosen as the standard temperature for the measurement of gas volumes. The operation of finding the volume at the standard temperature is called *correcting* the volume **Correcting for temperature.** Sometimes it is necessary to find the volume at a temperature other than the standard temperature. The operation is a similar one.

Example: A quantity of gas has a volume of 75 c.c. at a temperature of 24°. What will be its volume at 100°?

Since the temperature is increased, the volume will also be increased. The fraction by which the original volume is to be multiplied is therefore greater than one.

$$\begin{aligned}x &= 75 \text{ c.c.} \times \frac{373}{297} \\&= 94.2 \text{ c.c.}\end{aligned}$$

12. Boyle's Law.—Experiment shows that if the pressure on any gas is doubled and the temperature kept constant, the resulting volume will be one-half the original volume. Under a pressure three times as great, the volume is one-third. In general, the greater the pressure, the less the volume in a proportional degree. This generalization, known as Boyle's Law, is usually stated thus:

The temperature remaining the same, the volume of a gas varies inversely as the pressure exerted upon it.

13. Use of Boyle's Law in the Correction of Gas Volumes.—Boyle's Law, like Charles' Law, enables us to calculate the volume of a given quantity of gas under new conditions. For example, a quantity of gas has a volume of 120 c.c., the barometer standing at 740 mm. What will be the volume when the atmospheric pressure has increased until the barometer stands at 760 mm.?

The numbers 740 mm. and 760 mm. are measures of the two pressures. The new volume will be found by multiplying the original volume by the ratio of these two numbers. It is apparent that the gas will be subjected to a greater pressure under the new condition. According to the law its volume will be less. The fraction will therefore have the less number as the numerator. Hence:

$$\begin{aligned}x &= 120 \times \frac{740}{760} \\ &= 116.8 \text{ c.c.}\end{aligned}$$

The standard pressure for measuring gases is the pressure that the atmosphere exerts when the barometer stands at 760 mm. This is the average height of the barometer at sea-level. The operation of finding the volume of a gas at this pressure is called *correcting the gas for pressure*. The volume of a gas at any pressure whatever is found in a similar manner.

Example: A quantity of air measures 82.2 c.c. at 520 mm. pressure. What will be the volume at 800 mm., the temperature remaining constant?

It is evident that the resulting volume will be less than the original, since the pressure under the new condition is increased.

Hence the ratio by which the original volume is multiplied must be less than one.

$$\begin{aligned}x &= 82.2 \times \frac{520}{800} \\ &= 53.4 \text{ c.c.}\end{aligned}$$

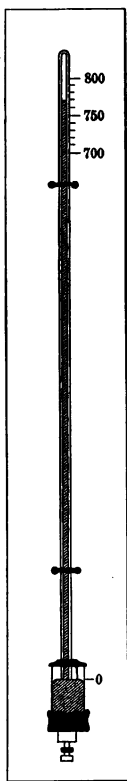


Fig. 3.
Barometer.

Simultaneous Correction for Temperature and Pressure. —

These two corrections can be carried out in one arithmetical operation, for the temperature effect and the pressure effect are entirely independent of each other. For example, a quantity of gas measures 206 c.c. at a temperature of 22° and a pressure of 750 mm. What will be the volume of the gas under standard conditions of temperature and pressure?

$$\begin{array}{rcccl}
 & & \text{Temperature} & \text{Pressure} & \\
 & & \text{correction.} & \text{correction.} & \\
 x = 206 & \times & \frac{273}{295} & \times & \frac{760}{750} \\
 & & = 188.1 \text{ c.c.} & &
 \end{array}$$

14. Correction for Difference in Level. — Gases are usually enclosed in bottles or tubes that stand over liquids. The liquid, as a rule, is either water or mercury. In order that the pressure of the gas enclosed under these conditions shall be equal to the atmospheric pressure, the levels of the liquid outside and inside the tube must be the same (Fig. 4). This condition is usually realized by adjusting the apparatus. Sometimes this is impossible, and then it is necessary to correct for the difference in level. This is done by adding to or subtracting from the height of the barometer a suitable number. When the inside level is the higher, the pressure on the enclosed gas is less than atmospheric (Fig. 5); when the inside level is the lower, the pressure is greater than atmospheric (Fig. 6). For mercury, the actual difference in millimeters is added or subtracted; for water, one-thirteenth

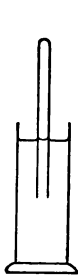


Fig. 4.

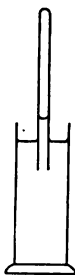


Fig. 5.

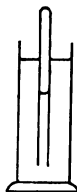


Fig. 6.

of this value is used, since water is about one-thirteenth as heavy as mercury.

Example: A volume of gas is enclosed in a tube over mercury (Fig. 7). The volume of gas measures 68.3 c.c., and the level of the mercury inside the tube is 114 mm. above the level in the dish. The thermometer reads 20° C. and the barometer 766 mm. Find the volume of the gas at standard conditions.

The corrected pressure is found by subtracting 114 mm. from 766 mm.,

$$766 - 114 = 652 \text{ mm.}$$

The gas volume will be corrected to standard conditions as follows:

$$\begin{aligned} x &= 68.3 \times \frac{273}{293} \times \frac{652}{760} \\ &= 54.6 \text{ c.c.} \end{aligned}$$

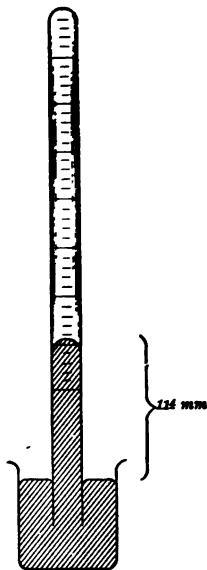


Fig. 7.

15. Correction for Pressure of Water Vapor.—A gas becomes saturated with water vapor if it is in contact with water. In such a case the pressure of the water vapor makes an appreciable part of the pressure that we are measuring, and its value must be subtracted from the observed barometric pressure in order to determine the pressure of the dry gas. The pressure of water vapor depends only on temperature, and not on any other conditions of the experiment. Hence it is always the same for the same temperature. Tables of these values for different temperatures have been prepared as the result of careful experiments. (See page 18.)

Corrections for difference in level and for the pressure of water vapor (sometimes called aqueous tension) are both pressure corrections. They are made by adding to or subtracting from the observed barometric pressure suitable numbers. They are parts, then, of the pressure correction.

Example: 24.6 c.c. of nitrogen is contained in a tube over water. The level of the water inside the tube is 27 mm. above the outside level. The barometer stands at 762 mm., and the thermometer at 23°. What is the corrected pressure? On consulting a table we find that the pressure of aqueous vapor at 23° is approximately 21 mm. The corrected pressure is therefore

$$762 - \overset{\text{Difference}}{\underset{\text{in level.}}{\frac{27}{18}}} - \overset{\text{Aqueous}}{\underset{\text{tension.}}{21}} = 739 \text{ mm.}$$

16. The following example will illustrate in full the operation of correcting gas volumes.

Volume of air	79.3 c.c.
Pressure uncorrected	764 mm.
Temperature	21°
Difference in level (water)	+ 41 mm.
Aqueous tension at 21°	18 mm.
Corrected pressure	
Corrected volume of air	

The corrected pressure is

$$764 - \overset{\text{Difference}}{\underset{\text{in level.}}{\frac{41}{18}}} - \overset{\text{Aqueous}}{\underset{\text{tension.}}{18}} = 743 \text{ mm.}$$

$$21^{\circ} \text{ C.} = 294^{\circ} \text{ abs.}$$

If the temperature of the gas were changed from 294° absolute to 273° absolute, its volume would become less. Hence the ratio for the temperature correction is $\frac{273}{294}$. Changing the pressure from 743 to 760 mm. would also tend to diminish the volume; the pressure correction ratio is, therefore, $\frac{743}{760}$.

$$\begin{aligned} x &= 79.3 \times \frac{273}{294} \times \frac{743}{760} \\ &= 71.9 \text{ c.c.} \end{aligned}$$

Problems.

1. A quantity of hydrogen measures 53 c.c. at a temperature of 20°. What would it measure at 28°?
2. 80.2 c.c. of air stand in a tube over water, the barometer stands at 768 mm.; the next day it reads 755 mm. What volume would the air then have?
3. 151 c.c. of nitrogen stand in a tube over water, with the inside level 139 mm. above the outside level. What volume would the gas have if the two levels were the same? The barometer stands at 754 mm.
4. How much would 52.2 c.c. of air measure if the barometric pressure changed from 750 mm. to 762 mm.? If the temperature also changed from 18° to 25°?
5. A quantity of air and water vapor, standing over water in a gas-measuring tube, levels adjusted, has a volume of 31.8 c.c. The temperature is 26°; the barometer stands at 737.6 mm. Correct the volume of air to standard conditions.
6. A quantity of air and water vapor in a tube over water, levels adjusted, measures 43 c.c. The thermometer stands at 24°, the barometer at 770 mm. Correct to standard conditions.

In the following cases correct the gas volume to standard conditions:

	VOLUME.	CONDITIONS.	TEMPERATURE.	BAROMETER.
7.	152 c.c.	Over mercury ; levels the same.	27°	755 mm.
8.	1.26 c.c.	Over water ; levels the same.	20°	748 mm.
9.	210 c.c.	Over water ; inside level 80 mm. above outside level.	22°	764 mm.
10.	15.2 c.c.	Over mercury ; inside level 30 mm. above outside level.	21°	760 mm.
11.	129 c.c.	Over water ; levels the same.	17°	770 mm.

12. A volume of gas (dry) measures 58.5 c.c. at a temperature of 183° and a barometric pressure of 759 mm. Find the volume of the gas under standard conditions.

13. In order to find the per cent of oxygen in air, the oxygen is absorbed by means of phosphorus, and the following data are obtained:

	ORIGINAL.	FINAL.
Volume	99.8 c.c.	77.0 c.c.
Temperature	24°	19°
Barometer	763 mm.	750 mm.

The air stands over water, and the levels are adjusted in reading both volumes. Determine the per cent of oxygen.

PRESSURE OF WATER VAPOR OR AQUEOUS TENSION

(in millimeters of mercury)

TEMPERATURE.	PRESSURE.	TEMPERATURE.	PRESSURE.
10.0° C.	9.2 mm.	20.0° C.	17.4 mm.
10.5	9.5	20.5	17.9
11.	9.8	21.	18.5
11.5	10.1	21.5	19.1
12.	10.5	22.	19.7
12.5	10.8	22.5	20.3
13.	11.2	23.	20.9
13.5	11.5	23.5	21.5
14.	11.9	24.	22.1
14.5	12.3	24.5	22.8
15.	12.7	25.	23.5
15.5	13.1	25.5	24.2
16.	13.5	26.	25.0
16.5	14.0	26.5	25.7
17.	14.4	27.	26.5
17.5	14.9	27.5	27.3
18.	15.4	28.	28.1
18.5	15.9	28.5	28.9
19.	16.4	29.	29.8
19.5	16.9	29.5	30.7
		30.	31.6

CHAPTER III.

OXYGEN.

17. Preparation. — In 1774, Priestley obtained oxygen from a red powder prepared by heating mercury in the air. If this powder be heated at a temperature somewhat higher than that at which it was prepared, it is decomposed into a gas (oxygen) and metallic mercury.

When pure oxygen is desired in quantity, it is usually prepared by heating potassium chlorate (Fig. 8), a com-

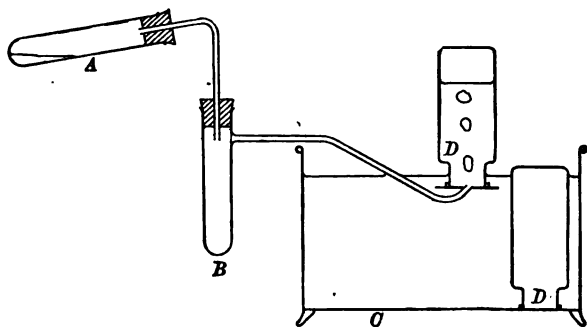


Fig. 8. Preparation of Oxygen.

A, tube containing potassium chlorate and manganese dioxide; *B*, safety tube; *C*, pneumatic trough; *D*, *D*, bottles for collecting the gas.

pound of potassium, chlorine, and oxygen; this, when heated, melts and gives oxygen gas and a residue of potassium chloride. In the laboratory it is customary to mix the potassium chlorate with manganese dioxide, as it is found that the decomposition is more regular and takes place at a lower temperature. A material which aids the decm-

position of another, without itself changing, is called a *catalytic agent*. To free the oxygen from dust and other impurities, it is allowed to bubble through water.

Oxygen may be prepared from water by passing an electric current through it.

18. Physical Properties. — Pure oxygen is a gas without color, taste, or odor. It is slightly more dense than air. It dissolves somewhat in water; under ordinary conditions, 100 volumes of water dissolve 3 volumes of oxygen. If ordinary faucet water be allowed to stand in a glass, or if the water be warmed, bubbles will be observed collected against the sides of the glass before the water actually boils. Such bubbles are largely oxygen, which was dissolved in the water. If cooled sufficiently, oxygen condenses to a pale blue liquid, and, on still further cooling, solidifies.

19. Chemical Properties. — The most noticeable chemical property of oxygen is its *tendency to combine with other elements*. At ordinary temperatures it does not readily react with many substances, but at higher temperatures its action is rapid, and is usually accompanied by heat and light. Nearly all the elements combine readily with oxygen to form compounds known as *oxides*.

Combustion is a chemical action by which heat and light are evolved. Lavoisier, in 1786, was the first to explain ordinary burning as the combining of a substance with oxygen. Heat is usually given off during such combinations. When the action takes place rapidly, the increase in temperature may be appreciable, and light may result. Thus, when a piece of coal burns, the carbon of the coal combines with the oxygen of the air to form carbon dioxide, a gas which

passes off unseen; at the same time a considerable quantity of heat is evolved, and the neighboring particles of fuel become red-hot.

As the air is only about one-fifth oxygen, substances do not burn as readily in it as in pure oxygen. A glowing splinter plunged into oxygen bursts into flame. Charcoal, which only glows in the air, burns rapidly in oxy-



Fig. 9. Phosphorus combining with oxygen.

gen. Sulphur burns in air with a pale blue flame, in oxygen brilliantly. Iron can be made to burn in oxygen with dazzling scintillations. A convenient method for burning solid substances in oxygen is to use a quick-sealing fruit jar and deflagrating spoon (Fig. 10).

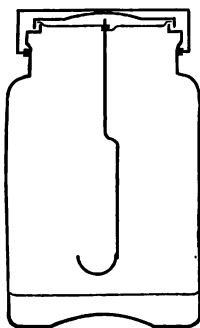


Fig. 10.

The combining action is not always accompanied by light or even by noticeable heat. Thus, when iron **Slow oxidation.** rusts, it slowly combines with

oxygen; when wood decays, the materials produced are nearly the same as are formed when it burns. The total amount of heat is the same in both cases, but in the decay the change takes so long a time that there is no appreciable change of temperature. A match gently rubbed in the dark, appears lumi-

nous without flaming. Such changes are termed *slow oxidation*, as distinguished from burning.

20. We know that some substances burn more easily than others; heat must be applied to raise them to the temperature at which they *take fire* and begin to burn.

Kindling temperature.

This *kindling temperature* varies with different substances; the kindling temperature of phosphorus is but little above the ordinary laboratory temperature, but the temperature produced by the burning is high. If the burning material is a good conductor, as iron, the heat is conducted away so rapidly that the temperature falls below the kindling temperature and the fire goes out. Similarly, gas lighted above

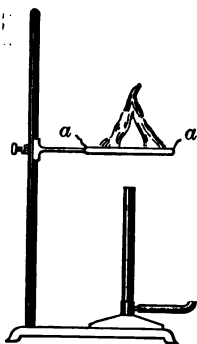


Fig. 11.

an iron gauze (*a*, Fig. 11) does not catch fire below the gauze, because the heat of the flame is conducted away by the iron. When the material is in small pieces, or is powdered, there is more surface exposed to the oxygen, so that the burning can proceed more rapidly; thus, finely divided iron will burn, since there is a large surface exposed, and there is no large mass to withdraw the heat. In the case of iron, the oxide produced is a solid which remains, and may cover the iron and prevent its coming in contact with the oxygen, thus stopping further action. Iron is artificially coated with a thin, regular film of oxide to protect the sheet against rusting. Iron so protected is known as Russia iron.

21. Many oils, such as are used in paints, absorb oxygen. Linseed oil absorbs oxygen and forms a tough, resinous substance, the skin seen on the surface of paint. On painted surfaces this skin holds the coloring matter and protects the material be-

Spontaneous combustion.

neath. The heat generated in its formation is dissipated in the air. If rags or waste, greasy with such oils, are left lying about, oxidation takes place, and since the materials are usually poor conductors and their form prevents sufficient circulation of the air to keep them cool, the heat does not escape, but accumulates until the temperature rises high enough for the stuff to take fire. Such cases of burning, started by the accumulation of the heat of a slow oxidation, are often called *spontaneous combustion*. It is especially liable to occur in poorly ventilated places and with greasy cloth and waste such as is used about machinery. Coal-dust often takes fire in this way in coal bunkers.

Since all common cases of burning depend on the presence of oxygen, the gas is said to *support combustion*.

22. Occurrence.—Oxygen is the most abundant element: about one-half of the solid crust of the earth, eight-ninths of the water, and one-fifth of the air, is oxygen. Limestone, marble, clay, quartz, and sand are nearly half oxygen, and it comprises a large proportion of animal and vegetable matter.

23. Oxygen in Relation to Life.—All animals need oxygen for the carrying on of their life processes. The air supplies this needed oxygen to land animals, while fishes obtain it from the dissolved oxygen which water absorbs from the air. The oxygen is taken in during the process of breathing, absorbed by the blood, and carried to all parts of the body. The various tissues are slowly oxidized, heat being liberated by the action. It is this heat which keeps the bodies of the higher animals continually warmer than the surrounding air. One of the chief

products of this oxidation is carbon dioxide, which is carried by the blood to the lungs and there exhaled.

Plants feed on carbon dioxide, which they absorb from the air through their leaves. The carbon of this compound is retained in the tissues of the plants, but the oxygen for the most part is returned to the air. Thus plants and animals mutually assist in keeping the quantity of oxygen in the air a constant quantity. Plants also inhale a small quantity of oxygen directly from the air, and exhale a little carbon dioxide.

24. Ozone.—If electric sparks are passed through oxygen, or better, if it be subjected to a “silent discharge,” it is changed to another form of oxygen, which is more active, and which has the irritating smell noticeable where electrical machinery is working. This form of oxygen is known as *ozone*.

Ozone is also produced when turpentine slowly evaporates and by the slow oxidation of phosphorus in moist air.

Silver, which is not affected by oxygen, is rapidly tarnished (oxidized) by ozone. Many colors are bleached by it (notice the cork of a turpentine bottle). Could it be cheaply prepared in quantity, it would be a useful disinfectant.

When ozone is heated to 250°C . it is changed to oxygen, two volumes of ozone yielding three volumes of oxygen, so that the ozone is one and a half times as dense as oxygen.

The atmosphere sometimes contains a small amount of ozone near the seashore and in the open country. The bleaching of flax and linen by exposing the goods on the grass in the early morning is attributed to the ozone dissolved in the dew.

Definitions.

A *catalytic agent* is a material which aids chemical action without itself being permanently changed.

An *oxide* is a compound of oxygen and another element.

Combustion is a chemical action in which heat and light are evolved.

Oxidation is the combination of a substance with oxygen.

Slow oxidation is the combination of a substance with oxygen without the accompaniment of light or noticeable heat.

The *kindling temperature* of a substance is the lowest temperature at which it takes fire and burns.

Exercises.

1. How would the production of oxygen be affected if potassium chlorate was heated without a catalytic agent?

2. What would happen if a lighted candle was lowered into a jar of oxygen? Why?

3. Explain why paper, wood, and coal are used in making a coal fire.

4. Why are metal cans provided for the oily waste in wood-turning shops?

5. Why should not the cloths used in wiping oily lamps be thrown into a closet?

6. Why may a spark in a flour mill produce an explosion?

7. How would you prove that water from a stream or a pond contains dissolved oxygen?

8. Account for the peculiar odor in the air after a thunderstorm.

9. Explain why polishing stoves prevents rusting.

10. Explain why a candle goes out if a wire gauze is slowly lowered till it touches the wick.

11. What two gases in the air are required by plants? Which in the larger amount?

CHAPTER IV.

HYDROGEN.

25. Preparation. — If the two wires from a battery be placed in pure water, it will be found that practically no current passes. Water is a very poor conductor of electricity. If a small quantity of sulphuric acid is added to the water, the solution is a good conductor. **Electrolysis of water.** During the passage of the current, bubbles form at the ends of the wires: at the positive electrode (anode) small bubbles of oxygen appear; at the negative electrode (cathode) there is a rapid evolution of hydrogen

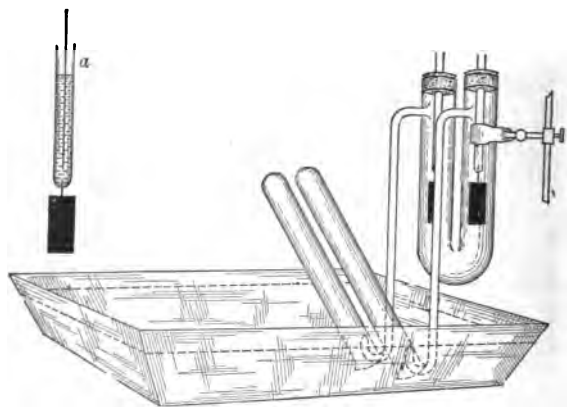


Fig. 12. Electrolysis of water.
a, platinum electrodes showing contact through mercury.

(Fig. 12). If the volumes of the gases be compared, it will be found that there has been twice as much hydrogen

set free as oxygen. The sulphuric acid is found unchanged in amount at the end of the experiment, while some of the water has disappeared. Other catalytic agents may be used instead of sulphuric acid. The electrolysis has practically converted the water into oxygen and hydrogen, the volume of which is very great compared with the volume of the water decomposed.

If a piece of potassium is placed on water, it skims rapidly back and forth over the surface, decomposing the water so rapidly that if a large piece of the metal is used, the action is dangerously violent. A great deal of heat is generated; usually the hydrogen set free ignites if air is present (Fig. 13). If sodium

**Action of
metals on
water.**



Fig. 13.

be used, although the action is very rapid, the heat generated is not usually sufficient to ignite the hydrogen unless

the water is warm. The metal sets free only one-half of the hydrogen of the water and combines with the remaining half and all of the oxygen to form the hydroxide of the metal. This dissolves in the excess of the water.

Potassium + water \rightarrow potassium hydroxide + hydrogen

Sodium + water \rightarrow sodium hydroxide + hydrogen

If calcium be used, the action is quiet, and the calcium hydroxide is not all dissolved. Magnesium will only act rapidly if the water is hot. If steam is passed through a heated iron pipe, filled with nails, an abundant supply of hydrogen can be obtained, all the oxygen of the steam combining with the iron.

Iron + water (steam) \rightarrow iron oxide + hydrogen

In the seventeenth century, Paracelsus observed that when iron dissolved in acids a gas was evolved.

All acids contain hydrogen and generally give it up in exchange for a metal, acting in this way somewhat like water. A water solution of hydrochloric or of sulphuric acid is commonly used, and the metal usually employed is zinc (Fig. 14). In the reaction, the hydrogen is set free and the metal combines with the acid residue to form a new material. Thus:

Replace-
ment in
acids by
metals.

Sulphuric acid + zinc \rightarrow zinc sulphate + hydrogen

{hydrogen
 sulphur
 oxygen

{zinc
 sulphur
 oxygen

Hydrochloric acid + zinc \rightarrow zinc chloride + hydrogen

{hydrogen
 chlorine

{zinc
 chlorine

This is the most convenient method, as the action is quiet and takes place at the ordinary temperature. The

rapidity of the action depends on the temperature, the concentration of the solution, the surface of the metal exposed, and the purity of the materials. If commercial zinc be used, some of the impurities are carried along with the hydrogen, giving it a peculiar, disagreeable smell. If iron is used instead of zinc, the unpleasant odor is more noticeable.

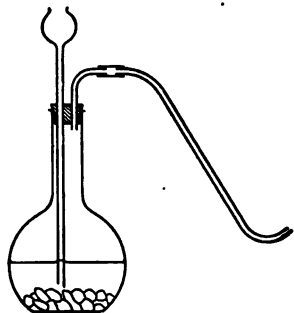


Fig. 14.

Hydrogen generator.

26. Physical Properties. — Hydrogen is without color, taste, or smell. It is the lightest substance known. Its specific gravity is very low, and it is scarcely soluble in water. The rate of escape of gases through minute apertures (effusion of gases) varies inversely as the square roots of the densities, and hydrogen, being the lightest gas, escapes more rapidly than any other. A small rubber balloon filled with hydrogen collapses more rapidly than a similar balloon filled with illuminating gas.

Certain metals, as platinum or palladium, have the power of absorbing a large volume of hydrogen. The hydrogen can be expelled from the metal by warming it. Such an absorption of a gas by a solid is called *occlusion*. While the gas is being absorbed, considerable heat is set free, and if oxygen is present, the hydrogen may ignite. The occluding action of such a metal is utilized in self-lighting burners and mantles.

Hydrogen has been liquefied and solidified. The liquid is one-fourteenth as dense as water, and is the lightest liquid known.

27. Chemical Properties.—The most important chemical property of hydrogen is its combustibility. Cavendish, in 1783, showed that hydrogen burning in air formed water (steam). The flame of hydrogen is blue, almost

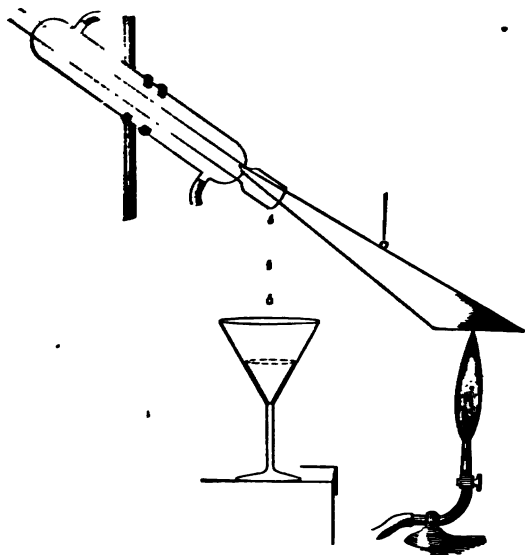


Fig. 15.
Metallic cone and condenser to cool water from burning hydrogen.

invisible in daylight, but very hot. Hydrogen, in burning, gives as much heat as five times its weight of coal. The water formed in the combustion usually passes off as steam, but may be condensed on a cool surface (Fig. 15).

If hydrogen and oxygen are mixed, and the mixture is raised to the kindling temperature, or a spark is applied, combustion takes place throughout the entire mixture almost instantaneously. Such a rapid combustion is called an *explosion*.

A jet of oxygen can be made to burn in hydrogen, thus showing that the gases take equal parts in the action. A lighted candle is extinguished in hydrogen.

When heated, hydrogen will combine with the oxygen of many oxides (Fig. 16), forming water (steam) and the metal, thus:



This process of taking oxygen away from a substance is called *reduction*, and substances that take oxygen away are called *reducing agents*. As the hydrogen is *oxidized* in the process, we see that oxidation and reduction go on together and are opposite processes. Hydrogen is one of the most energetic reducing agents, and the great amount of energy evolved on the formation of water explains the stability of water. Energy equivalent to 3800 calories of heat must be used to decompose one gram of water into hydrogen and oxygen.

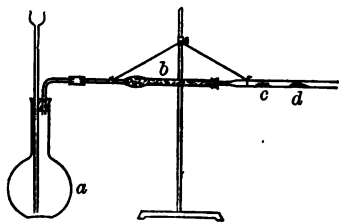


Fig. 16.

Reduction of hot copper oxide by hydrogen.

a, hydrogen generator; *b*, drying tube; *c*, copper oxide; *d*, anhydrous copper sulphate, test for water.

the tip, then the oxygen is turned on through the inner tube. As the gases are supplied under pressure, a blast is formed which gives an intense heat. This flame is used

28. **Uses.**—The low density of hydrogen permits its use in balloons. The high temperature of the flame is used in the oxy-hydrogen blowpipe. This consists of two tubes as shown in Figure 17. The hydrogen passes through the outer and is lighted at



Fig. 17.

Oxy-hydrogen blowpipe.

to melt platinum and other refractory materials. When a stick of quicklime is placed in the tip of the flame, it does not melt, but becomes white-hot, giving an intense white light. This is known as the Drummond, lime, or calcium light.

The process of joining sheets of lead, edge to edge, known as lead-burning, consists in laying the sheets in the position desired and melting the edges together with a hydrogen flame.

Ordinary water-gas, used in illuminating, contains about forty per cent of hydrogen. It is prepared by blowing steam through a mass of incandescent anthracite coal or coke.

Summary.

Hydrogen is commonly prepared by :

- (1) the electrolysis of water ;
- (2) the reaction between water and a metal ;
- (3) replacement in an acid by a metal. This is the most convenient method.

A liter of hydrogen, under standard conditions, weighs 0.09 gram. A liter of water at 20° dissolves 18.4 c.c. of hydrogen. Liquid hydrogen boils at -252.5° and solidifies at -256° .

Hydrogen burns in oxygen or air, forming water. It is a powerful reducing agent. The chief uses of hydrogen are for balloons and fuel.

Exercises.

1. What would be the result of collecting together the gases formed by the electrolysis of water and applying a light to the mixture ?
2. Would you use water or sand to extinguish burning potassium ? Why ?

3. Would you use zinc or iron for making hydrogen to fill a large balloon? Why?

4. What becomes of the product, other than hydrogen, formed when zinc and sulphuric acid react?

5. Is water an oxide?

6. How would a soap-bubble behave if filled with hydrogen instead of air?

7. Why must all the air be expelled from a hydrogen generator before the gas is lighted at the end of the delivery tube?

8. Should vessels containing hydrogen be kept mouth upward or mouth downward?

9. Why would pure hydrogen not make a good illuminating gas?

10. Could hydrogen be substituted for illuminating gas in a gas stove?

11. What is formed when iron oxide is heated in a current of hydrogen?

12. Would a Welsbach burner supplied with hydrogen give light?

13. Why is it particularly important that all the joints of a hydrogen apparatus be tight?

14. Would a bottle of hydrogen, closed with an ordinary cork, remain full after standing overnight?

15. Would a bottle of hydrogen remain full if left inverted overnight with its mouth under water?

CHAPTER V.

COMPOSITION OF WATER AND COMBINING WEIGHTS.

29. Determination of Composition. — In the electrolysis of water we showed that water could be separated into two parts hydrogen and one part oxygen by volume.

Analysis. Such a separation is called an *analysis*. The combining of these substances is called a *synthesis* of water.

If a known volume of hydrogen and oxygen are introduced into a tube inverted over mercury, and exploded by

Synthesis: an electric spark between platinum wires fused volumetric. through the glass, it is found that the volumes of the gases used up are two volumes of hydrogen to one

of oxygen, and that any excess of either gas is left unchanged. It is only when two volumes of hydrogen are mixed with one of oxygen that the two gases totally disappear. A little mist is seen on the tube, which is the moisture formed, and the mercury rises and fills the tube. This, again, shows that water consists of two parts hydrogen and one part oxygen.

Another form of apparatus (Fig. 18), differing in the shape of the tube from that just described, facilitates the adjustment and reading of the mercury

levels. Additional mercury, if needed, can be poured

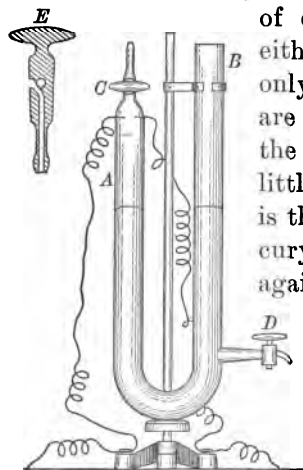


Fig. 18.

through the open arm *B* and an excess drawn off through the lower stopcock *D*. The gases used in *A* can be drawn in easily through the three-way stopcock *C* shown in detail at *E*.

If dry hydrogen is passed over a weighed quantity of copper oxide which is heated, steam and copper result (Fig. 19). The water can be collected and weighed in a tube containing a drying agent. The **Synthesis:** weight lost by the copper oxide is the weight **gravimetric.** of the oxygen. The difference between the weight of the oxygen and the weight of the water formed is the weight of the hydrogen.

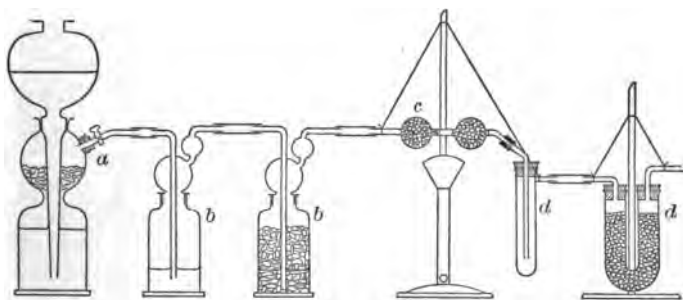


Fig. 19.

Composition of water by weight.

a, hydrogen generator ; *b, b*, drying bottles containing concentrated sulphuric acid ;
c, ignition tube containing copper oxide ; *d, d*, apparatus for collecting water formed.

The ratio between the weights of the oxygen and hydrogen is found to be 7.94 : 1. This relation is unvarying. Experience has shown that every **Law of** compound has a definite composition by weight. **definite** This is known as Dalton's first law, or the **law** **proportions.** of definite proportions.

30. Combining Weights.—Experience has shown that the

knowledge of the composition by weight of chemical compounds is very useful. For example, we can determine what weights of substances are needed for a given chemical action, and what weight of the products will be formed. Moreover, a study of these weights reveals some surprising regularities. Let us consider a few simple cases: hydrogen combines readily with chlorine and bromine. The ratios of the combining weights in the two cases are:

(*a*) weight of hydrogen : weight of chlorine :: 1 : 35.5.

(*b*) weight of hydrogen : weight of bromine :: 1 : 80.

Sodium and potassium also form compounds with chlorine and bromine; the ratios in these cases are:

(*c*) weight of sodium : weight of chlorine :: 1 : 1.54.

(*d*) weight of sodium : weight of bromine :: 1 : 3.47.

(*e*) weight of potassium : weight of chlorine :: 1 : 0.91.

(*f*) weight of potassium : weight of bromine :: 1 : 2.05.

In combining with hydrogen (see *a* and *b*):

weight of bromine : weight of chlorine :: 80 : 35.5, or $2.25 : 1$.

$$\frac{80}{35.5} = 2.25.$$

In combining with sodium (see *c* and *d*):

weight of bromine : weight of chlorine :: 3.47 : 1.54, or $2.25 : 1$.

In combining with potassium (see *e* and *f*):

weight of bromine : weight of chlorine :: 2.05 : 0.91, or $2.25 : 1$.

An examination shows the ratio of bromine to chlorine to be the same in each of the three kinds of compounds, that is, $2.25 : 1$. This suggests the value of reducing all the ratios to a common standard, so that the regularities will be apparent at a glance. Hydrogen enters into combination in the least part by weight of any of the elements.

Let us, therefore, use 1 for the combining weight of this element. It follows, then, from (a) and (b) that the number for chlorine will be 35.5; for bromine, 80. In the case of the sodium compounds it will be necessary to multiply the ratio (c) by such a number that the number for chlorine becomes 35.5; ratio (d) by such a number that the number for bromine becomes 80. (The multiplier for ratio (c) is found by dividing 35.5 by 1.54, which gives 23; the multiplier for ratio (d) by dividing 80 by 3.47, which gives 23.)

Multiplying ratios (c) and (d) we have

(g) weight of sodium : weight of chlorine :: 23 : 35.5.

(h) weight of sodium : weight of bromine :: 23 : 80.

In a similar manner from ratios (e) and (f) we can derive the ratios:

(i) weight of potassium : weight of chlorine :: 39 : 35.5.

(j) weight of potassium : weight of bromine :: 39 : 80.

Thus we see that the combining number is found to be the same for each of these elements, regardless of the other element in the compound. Experiment shows that twenty-three grams of sodium or thirty-nine grams of potassium are required to liberate one gram of hydrogen from water or any other hydrogen compound. From this it appears that each element enters into chemical action in a definite number of parts by weight, and if we establish these numbers on a relative scale, the number for an element is the same in all its compounds. This number is called the *equivalent* or *reacting weight* of the element.

31. Reacting Weight. — It is found that such a number can be assigned to every element. The number is found by determining the number of parts by weight of the given

element which unite with, or replace, one part of hydrogen, or its equivalent. Thus we see that all reacting weights are relative numbers, and they refer or relate to the combining weight of hydrogen which is taken as unity.

It frequently happens that more than one reacting weight can be assigned to a given element. For instance, oxygen combines in two different proportions with hydrogen, forming two different compounds. In water the ratio is 8 to 1, in the other compound the ratio is 16 to 1. In such cases, one number is always a multiple of the other.

32. Method of determining Reacting Weights. — The reacting weight is determined by an analysis of the hydrogen compound, if one exists. In some other cases the value is determined by finding the weight of the element that replaces 1 gram of hydrogen. In still other cases, the number expressing the weight of the element that combines with 35.5 grams of chlorine or 8 grams of oxygen is taken as the reacting weight.

Summary.

The composition of water can be shown by analysis and by synthesis. Two volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

Water consists of 1 part by weight of hydrogen combined with 8 parts of oxygen; and it illustrates the law of definite proportions, since it always has this composition.

The number of parts by weight of an element which react with one part by weight of hydrogen, or its equivalent, is called the *reacting weight* of that element. When an element has more than one reacting weight, the numbers expressing these weights are always multiples of the smallest number.

Exercises.

1. When sugar is heated sufficiently to char it, water is driven off. What two elements besides carbon must sugar contain?

2. Why does a thin film of water collect on the inside of a lamp chimney when the lamp is first lighted? Why does the moisture soon disappear?

3. Dry hydrogen was passed over heated copper oxide and the water formed absorbed by fused calcium chloride. The following results were obtained:

Wt. of copper oxide tube before the experiment . . . 70 g.

Wt. of copper oxide tube after the experiment. . . . 66 g.

Wt. of calcium chloride tube after the experiment . 106.5 g.

Wt. of calcium chloride tube before the experiment . 102 g.

From the above data calculate the weight composition of water.

4. 15 c.c. of oxygen were collected in a eudiometer over mercury. Dry hydrogen was passed into the eudiometer until the volume of the mixed gas was 22.4 c.c. A spark was then passed through the mixture. What gas was left in the eudiometer? How would you prove your answer? What would be the volume of the remaining gas?

5. Mention three ways by which water can be decomposed.

6. What does the analysis of water show its composition to be by volume?

7. Mention two methods for the synthesis of water.

CHAPTER VI.

WATER AND SOLUTION.

33. Physical Properties.—Pure water is an odorless liquid. Small quantities appear to be colorless, although large masses show a distinct blue color. Water is usually taken as the standard in comparisons of physical properties of liquids and solids. The zero of the Centigrade thermometer registers the position of the top of the mercury column when the thermometer is placed in melting ice, and since a pure substance on being warmed always melts at the same temperature as that at which it would solidify if cooled, the zero of the Centigrade thermometer is the freezing-point for water.

When pure water is heated to 100°C . it boils; if we continue to apply heat, the temperature does not rise higher, provided the steam is allowed to escape. The heat used in converting water into steam is known as the *heat of vaporization*, or the latent heat of steam; it is given off when the steam condenses. Seventy-nine heat units are required to change a unit mass of ice to water, and 536 heat units are needed to change the same mass of water to steam. The heat unit is $\frac{1}{180}$ of the quantity of heat required to raise a unit mass of water from 0°C . to 100°C .

Both the freezing and boiling temperatures change when the pressure changes; increased pressure raises the boiling-point and lowers the freezing-point, in both cases tending to keep it in the *liquid* form. Any dissolved solid acts in the same way.

34. Distillation. — All natural water contains dissolved substances. It is therefore necessary to boil water and then condense the steam to make it fit for chemical use; this process is called *distillation* (Fig. 20). Solids and

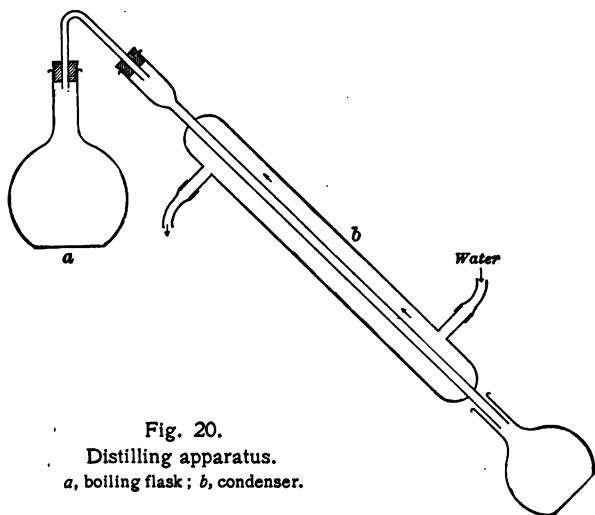


Fig. 20.
Distilling apparatus.
a, boiling flask; *b*, condenser.

liquids with boiling-points higher than that of water would be left behind, as the temperature of the steam remains the same during the distillation. Materials having lower boiling-points than water would be distilled before or with the water; such impurities, as ammonia, are found in the first portion of the condensed steam, and this is rejected.

35. Steam. — Steam is water in the gaseous state; at ordinary pressure it condenses to liquid at $100^{\circ}\text{C}.$; if the pressure were removed, it would remain in the gaseous condition at lower temperatures. The volume of steam is about 1600 times that of the water from which it was formed.

36. Ice.—If the temperature of the water is lowered to 0° C., and energy removed, it solidifies to ice, usually crystallizing in hexagonal clusters of needles. There is considerable expansion during the solidification, and the density of the ice is only 0.91 that of water.

Water requires more heat to raise its temperature than do most substances; therefore its temperature changes more slowly than most substances, and large masses of water have a determining influence on the climate of the neighboring land.

37. Solution.—The most important property of water is its ability to dissolve substances. A substance is said to be in solution in a liquid when it is distributed uniformly through the liquid in a state of such fine division that its particles cannot be seen, and do not settle out on standing. When the particles are visible, the substance is said to be in suspension, and will usually settle quickly. A liquid used to dissolve a substance is called a *solvent*; the dissolved substance is termed the *solute*. A solution will not boil at the same temperature as the solvent, nor will their freezing-points be the same.

Water is a solvent for a large number of substances and this use is most important. It dissolves both gases and solids and mixes with many liquids. Liquids which do not separate but form a uniform mixture when brought together, as alcohol and water, or glycerine and water, are said to be *miscible*.

Saturation.—A solution is not a definite compound. A small portion of salt may be dissolved in a large quantity of water; such a solution is said to be *dilute*. In a dilute solution, the substance is as uniformly distributed in all

parts of the liquid as it is in one containing a much larger proportion of the dissolved substance. A definite amount of water will dissolve any amount of a given solid up to a fixed quantity. If a liter of water at 20° C. is taken, it is possible to dissolve in it any weight of salt up to 360 grams. When the water has dissolved all the salt it can under given conditions, it is said to be *saturated* with salt at the temperature mentioned. A similar statement can be made concerning the solubility of any solid in any liquid. When any solvent has dissolved all of a given solute it can, under definite conditions, it is said to be *saturated with respect to that substance under the conditions named*. A solution saturated with one substance may dissolve other substances. Thus, water saturated with respect to salt can dissolve saltpeter.

38. Solubility Factors.—The solubility of most substances is decidedly affected by the temperature. Solids are usually, *but not always*, more soluble in liquids at high than at low temperatures. Sugar and alum are more soluble in hot water than in cold. Salt dissolves nearly as well in cold as in hot water. Calcium hydroxide, used in the preparation of lime-water, is more soluble in cold water than in warm.

Unlike solids, the solubility of gases in liquids decreases as the temperature rises. Ammonia and carbon dioxide are less soluble in hot water than they are in cold. Different substances differ very much in their solubility in a given solvent, and different solvents differ in their power to dissolve the same substance.

39. Freezing Mixtures.—There are important energy changes during solution. When a solid is dissolved,

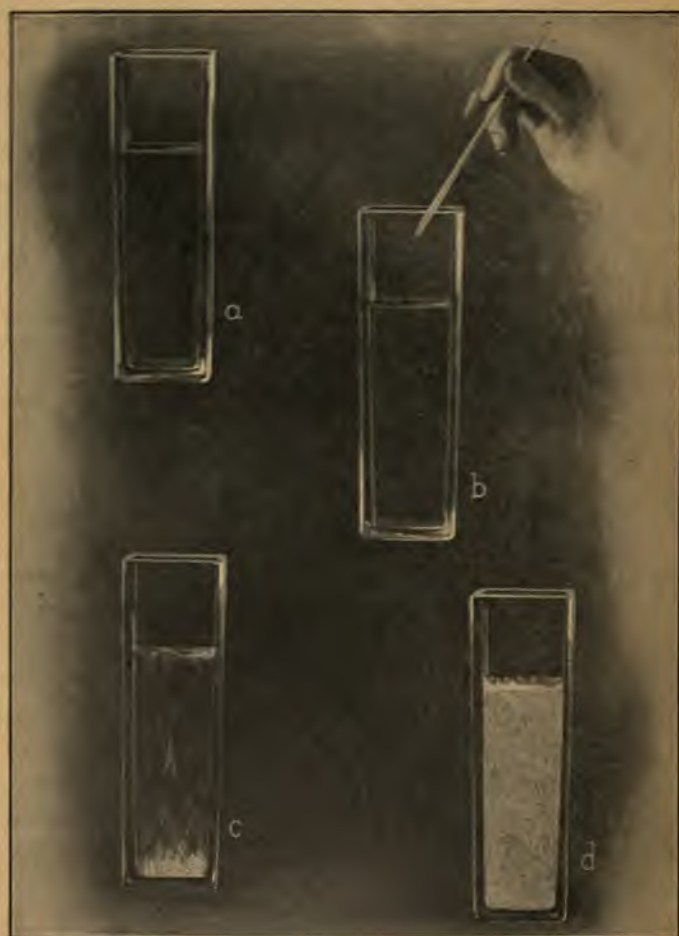


Fig. 21.
Crystallization of a supersaturated solution.

energy is absorbed and there is generally a fall in temperature. This is made use of in freezing mixtures. When ice and salt are mixed, some of the ice melts and the salt dissolves in the water. Both processes result in the absorption of heat, and the temperature of the mixture falls considerably below the freezing point of pure water. When equal parts of ammonium nitrate and water are mixed, at 0°C ., the temperature falls to -15°C .

40. Supersaturation. — If a solution is saturated at a high temperature and then allowed to cool slowly without any disturbance, it will often cool to a much lower temperature without depositing any of the substance dissolved (Fig. 21, *a*). But if a particle of the dissolved substance is dropped into the solution, a sudden crystallization takes place, accompanied by an evolution of heat (Fig. 21, *b, c, d*). Such a solution is said to have been *supersaturated at the lower temperature*. Any disturbance is liable to produce the crystallization.

41. Crystals. — The fact that the solubility varies with the temperature is made use of in separating solids from solution. If a solution which is saturated at a high temperature be allowed to cool slowly, the dissolved substance will often separate into definite forms called *crystals*. Crystals are usually transparent and symmetrical (Fig. 22). By the evaporation of the solvent, crystals may be obtained from the dilute solution of a solid.

42. Water of Crystallization. — Many substances in crystallizing from aqueous solutions unite with a definite quantity of water which is necessary to the shape of the crystal. This water is called *water of crystallization*. Copper sulphate or blue vitriol contains water of crystal-

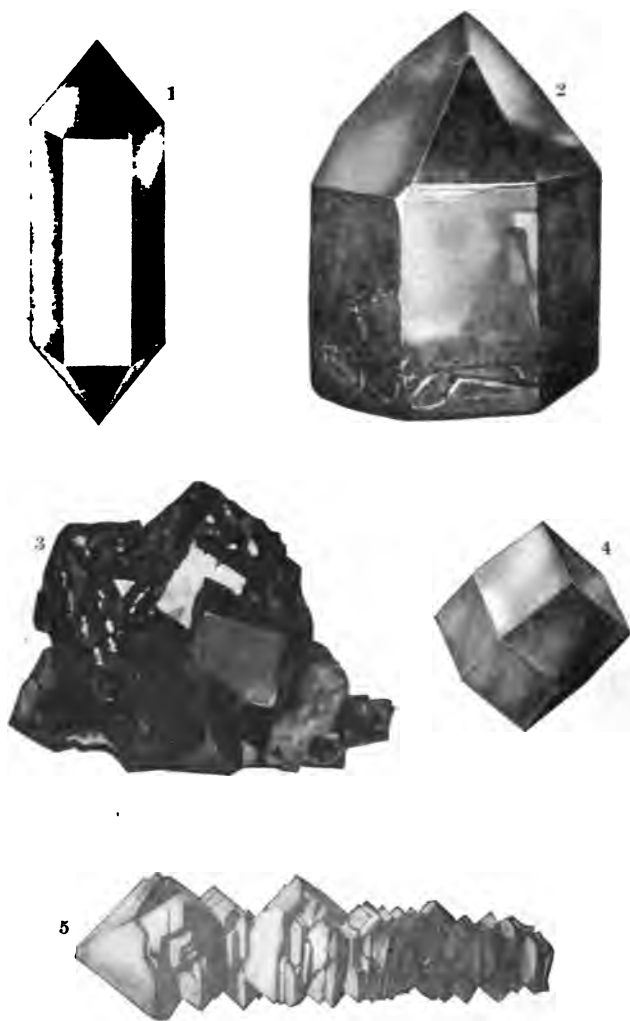


Fig. 22.

Crystals of familiar substances.

1. Quartz (ideal). 2. Quartz (actual). 3. Galena or lead sulphide. 4. Garnet. 5. Alum.

lization, and if it is heated in a test-tube, moisture will be seen on the cooler portions of the tube and the blue crystal will change to a white powder. The heating has driven off the water of crystallization.

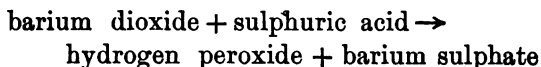
43. Efflorescence and Deliquescence.—If a crystal of washing soda is exposed to the air in a dry place, it will lose its water of crystallization and become covered with a fine powder. Such a material is said to be *efflorescent*.

Many materials, as lime, calcium chloride, and caustic potash, usually absorb moisture from the air and are therefore said to be *hygroscopic*. If they absorb sufficient moisture to dissolve them or to become *wet*, they are said to be *deliquescent*. Such materials are useful in drying others. Whether a substance will give up its moisture to the air or will absorb moisture, depends largely on the amount of moisture already in the air and also on the temperature.

HYDROGEN PEROXIDE.

Hydrogen and oxygen form a compound other than water in which the weights of hydrogen and oxygen are as 1 to 16. As it contains more oxygen for a given amount of hydrogen than water, it is called hydrogen peroxide, or hydrogen dioxide.

44. Preparation.—Hydrogen peroxide is prepared by treating barium dioxide with dilute sulphuric acid. The reaction taking place may be represented :



45. Properties.—Hydrogen peroxide is a clear, syrupy liquid, heavier than water and miscible with it. Its most

important chemical property is the ease with which it gives up part of its oxygen. The other product of the decomposition is water.

hydrogen peroxide \rightarrow water + oxygen

46. Uses. — As hydrogen peroxide readily gives up half of its oxygen, it is a valuable oxidizing agent, and most of its uses depend on this fact. It is seldom prepared pure, and is always used in solution. The commercial solution contains about 3 per cent of the dioxide.

It is used as a disinfectant, in washing wounds and sores, as it oxidizes dead and decomposing matter. It has but little action on living tissue, and as only water remains after its decomposition, it does not produce irritation and poisoning as do many other disinfectants.

It destroys the coloring matter of hair and woollen goods and in this way bleaches them. In many of its actions it resembles ozone.

47. Law of Multiple Proportions. — In water the weights of the hydrogen and oxygen are in the ratio of one to eight. In hydrogen peroxide the ratio is 1 to 16. Thus the hydrogen in the peroxide is combined with twice as much oxygen as the hydrogen of the water. A similar relation is found in many cases. *Whenever two substances, A and B, unite to form more than one compound, if we consider a fixed weight of A, the weights of B which combine with it, are integral multiples of one another.* This is known as the *law of multiple proportions* or Dalton's second law.

Summary.

Water is the standard for specific gravity and for the specific heat of liquids and solids. Its freezing-point and its boiling-point are respectively 0° and 100° on the Centigrade thermometer.

Water can be purified by filtration, distillation, and freezing.

It is the most common solvent. The amount of a solute in a given quantity of a solvent causes a solution to be either unsaturated, saturated, or supersaturated. Important temperature changes take place during solution.

Most substances are either hygroscopic, deliquescent, or efflorescent. Many compounds contain water of crystallization.

Hydrogen Peroxide can be prepared by the addition of barium peroxide to cold dilute sulphuric acid or to dilute hydrochloric acid. Hydrogen dioxide is a strong oxidizing agent and is used as a germicide and for bleaching.

Hydrogen peroxide consists of 1 part by weight of hydrogen combined with 16 parts by weight of oxygen.

The composition of water and of hydrogen dioxide illustrate the *law of multiple proportions*.

Exercises.

1. Why does water put out fire?
2. Is ammonia more soluble in cold or in hot water?
3. Water is saturated with soda at a high temperature and the solution allowed to cool. Would the solution then be saturated?
4. How could you determine whether a certain solution is saturated, unsaturated, or supersaturated?
5. How could a supersaturated solution of "hypo" be prepared?
6. Why do crystals of washing soda become covered with a coating of white powder when exposed to air?
7. How does a hygroscopic substance differ from a deliquescent substance?
8. Why is fused calcium chloride used as a drying agent?
9. How does a solution differ from a chemical compound?

10. When sea-water is evaporated, why does one of the substances in solution commence to separate before the others?

11. How would you show that any natural water is a dilute solution?

12. Mention three ways by which water can be purified.

13. If sold at the same price per pound, would it be more economical to buy washing soda before or after it has been exposed to the air for some time?

14. Show how the composition of water and hydrogen peroxide illustrate the law of multiple proportions.

15. Why does not a solution of hydrogen peroxide keep well when exposed to the air?

CHAPTER VII.

ATOMS AND MOLECULES.

48. Law of Conservation of Matter. — We have studied several substances and some of the laws governing the quantities of matter that take part in chemical actions, without attempting any description of the structure or make-up of the materials used.

Matter is generally defined as anything which takes up room. The different kinds of matter are called *substances*. So far as we know, *matter is indestructible*, nor has any one succeeded in making something from nothing. We may *change its properties*, but we always have the *same amount of matter* after the change as before.

49. Atomic Hypothesis. — We found that the combining or reacting weights are different for various elements but are constant or unchanging for each element. There is apparently something significant in the fact that in the compounds of oxygen the amount of oxygen combined with a given weight of hydrogen is eight, or twice eight, times the weight of the hydrogen.

Since water is composed of eight parts oxygen and one part of hydrogen, the smallest masses of water must have this composition. For the same reason, the smallest masses of hydrogen peroxide must contain sixteen parts of oxygen to one of hydrogen. There must be some reason why this number eight is characteristic of oxygen, and why there is no compound of these elements in which the ratio is twelve to one or twenty to one.

John Dalton in 1805 made certain assumptions, known as the *atomic hypothesis*, by which we can readily explain these facts. These assumptions were:

1st, matter is made up of small particles;

2d, these particles possess the power of attracting or holding on to other particles;

3d, these particles do not subdivide in taking part in chemical changes.

These particles, which do not divide in chemical changes, are called *atoms*. Different kinds of atoms

Atoms. may differ in weight, form, and combining power,

but all atoms of the same material must be alike. All the atoms of hydrogen are alike, all the atoms of oxygen are alike. We have found that when oxygen and hydrogen combine a substance is formed which possesses properties differing from either. The smallest conceivable quantity of oxygen will possess the same properties as a mass of oxygen which we can observe; the same will be true of the smallest mass of hydrogen, and of the smallest mass of the product, water. If we assume that each atom of oxygen is accompanied by an atom of hydrogen that always holds on to it; the mass made up of such a pair of minute particles does not have the properties of hydrogen or of oxygen. It is a new kind of substance—an oxide of hydrogen. The smallest conceivable quantity of this substance contains both hydrogen and oxygen.

The smallest quantity of a substance, having the properties of the mass is called a *molecule*. An atom is the

Molecules. smallest subdivision of an element. Molecules

are usually aggregations of atoms. The molecule is the physical unit of the mass, as the atoms comprising it do not usually separate during *physical* changes.

50. Explanation of the Law of Definite Proportions.— Suppose one atom of an element, *e.g.* hydrogen, combines with one atom of another element, *e.g.* oxygen, to form a molecule; then any considerable quantity of hydrogen oxide would be made up of a great number of such molecules. The weight of the hydrogen oxide would be the sum of the weights of the atoms composing it.

If we assume that the mass of the oxygen atom is eight times that of the hydrogen atom, it follows that in the mass of the oxide the ratio of the oxygen to the hydrogen must be *eight* to one, since equal numbers of the atoms of each element were used in the combination. Suppose, however, an effort is made to cause 8.3 grams of oxygen to unite with 1 gram of hydrogen. These weights will not contain equal numbers of atoms; the mass of the oxygen will contain the larger number. Consequently, when combination takes place, a number of oxygen atoms will remain unused. The mass of oxygen that has combined will weigh exactly eight times as much as the hydrogen. The 0.3 gram excess of oxygen will remain uncombined.

Whatever the weight of the atoms may be, chemical action *must* take place between definite masses of substances, and the composition of a compound must be definite. The law of definite proportions, then, is explained by assuming that chemical combinations always take place between atoms.

51. Explanation of the Law of Multiple Proportions.— If the hydrogen oxide molecule is composed of one atom of hydrogen and one atom of oxygen, we can imagine combinations of one atom of hydrogen with two, three, or more oxygen atoms. Whatever the combination may be, it is

evident from the atomic hypothesis that the weight of oxygen combined with a certain quantity of hydrogen *must* be an integral multiple of the amount which combines with the hydrogen to form hydrogen oxide.

The reacting weights are ratios between the weights of different kinds of atoms, or multiples of these weights. If we knew that in water one atom of oxygen was combined with one atom of hydrogen, *as we assumed*, the weight of the oxygen atom would be eight times that of the hydrogen atom. If, however, there are *two* atoms of hydrogen to each oxygen atom, the one atom of oxygen must weigh *sixteen* times as much as one atom of hydrogen. If there are *two oxygen* atoms to each hydrogen atom, each oxygen atom would be *four* times as heavy as the one hydrogen atom.

If we know how many of each kind of atom there are in a molecule, we can find the relative weights of the atoms. Such determinations have been made by comparison of physical properties.

52. Value of Atomic Hypothesis.—The atomic hypothesis gives a convenient way of explaining the facts upon which the laws of definite and multiple proportions are based. We must not forget, however, that the *laws are statements of facts, based on experimental evidence*, while the atomic hypothesis is used in the attempt to picture a structure or process which would agree with the facts. We do not know that this *is* the way that matter is made up. Perhaps in time a better explanation, based on different suppositions, may be offered, but we do know that it has proved useful in explaining a wide variety of facts and has done more than any other theory for the advancement of chemistry. Practically all scientific explanations of chemical phenomena are based on this hypothesis.

Summary.

Matter is anything that takes up room. It is indestructible. Its properties may be changed, but there is always the same amount of matter after a change as before.

The study of the weight relations of chemical changes shows that each element has its definite combining or reacting weight. The amount of any element found in chemical compounds is either this reacting weight or some multiple of it.

These facts are explained by the *atomic hypothesis*. This assumes matter to be made up of small particles which attract or hold on to other particles, but which do not subdivide in chemical changes.

Atoms are the particles indivisible in chemical changes. All the atoms of an element are alike and possess the characteristic properties of that element, but differ from the atoms of all other elements. A *molecule* is the smallest quantity of a substance having the properties of the mass.

The atomic hypothesis gives a convenient explanation of the facts upon which the laws of definite and multiple proportions are based. It has been the most valuable theory in the establishment of chemistry as a science. Sometime a better explanation may replace this hypothesis.

Exercises.

1. Why must an extended study of the composition of substances be made before the atomic hypothesis can be accepted?

2. Mercury is put into a glass flask which is then sealed, weighed, heated, and weighed again. Why is there no change in the weight although the mercury turns to a red powder?

3. Why is it that the attempt to make 35.5 grams of chlorine combine with 24 grams sodium, always leaves 1 gram of sodium uncombined?

4. Dalton knew that one oxide of carbon contained $2\frac{2}{3}$ parts of oxygen to 1 part of carbon and that another oxide was composed of $1\frac{1}{3}$ parts of oxygen to 1 part of carbon. What law do these two facts illustrate? Explain them according to the atomic hypothesis.

5. Why is the molecule of more importance in physics than in chemistry?

6. Why was not the present atomic hypothesis evolved before the time of Lavoisier?

7. Dalton showed that for one part by weight of hydrogen, olefiant gas contained twice as many parts by weight of carbon as marsh gas. Explain these facts according to the atomic hypothesis.

8. Explain this statement: "Without the atomic conception, chemistry would be a chaos of unrelated facts; with the theory, it has become an orderly science" (T. W. Clarke).

CHAPTER VIII.

CHLORINE.

53. Chlorine may be said to be a typical non-metallic element. It displays in a marked degree those properties which are regarded as characteristic of the non-metals. The most abundant compound of chlorine found in nature is sodium chloride, common salt. Sodium chloride is a very stable compound ; heat does not decompose it except at an extremely high temperature. Chlorine can be obtained from it in several ways.

54. Preparation. — An electric current can be passed through a solution of common salt, using apparatus similar to that used in the electrolysis of water. The electrodes in this case, however, should be of carbon, since platinum might combine with the chlorine which is evolved. The apparatus is filled with a concentrated solution of salt. When the current passes, chlorine is evolved as a gas at the anode and hydrogen at the cathode. Sodium is probably first liberated at the cathode ; but since this element reacts rapidly with water, it is impossible for it to accumulate. Hydrogen is set free as a result of the action of sodium with water.

Sodium chloride \longrightarrow sodium + chlorine

Sodium + water \longrightarrow hydrogen + sodium hydroxide

As the final products we have the two gases, hydrogen and chlorine, and sodium hydroxide which is dissolved in the water.

Hydrochloric acid is a compound of hydrogen and chlorine. The chlorine might be separated by electrolysis, but it is more usual to take advantage of the fact that hydrogen has a great tendency to combine with oxygen; so that if we oxidize hydrochloric acid, the hydrogen will combine with the oxygen to form water, and free chlorine will be obtained. **Oxidation of hydrochloric acid.** Oxygen from the air might be used. Hydrochloric acid (gas) and air are passed through a heated tube containing a catalytic agent. The action is slow and can be well carried out only on a large scale.

In the laboratory, manganese dioxide is the oxidizing agent usually employed. Concentrated hydrochloric acid solution is mixed with manganese dioxide; when the mixture is warmed, chlorine is evolved (Fig. 23). The

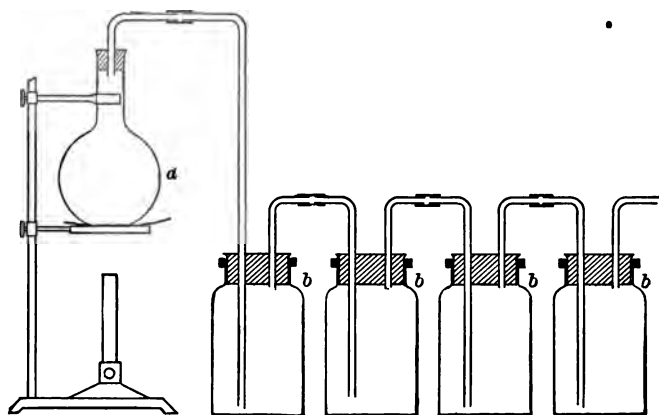
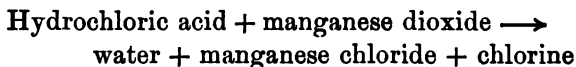


Fig. 23. Preparation of chlorine.

a, generating flask; *b*, bottles for collection of gas.

hydrogen of the acid combines with the oxygen of the dioxide, forming water. The manganese combines with

half the chlorine of the acid, forming manganese chloride, which dissolves in the water; the remaining portion of the chlorine is evolved as a gas.



The chlorine is not usually collected over water, since dry chlorine is desirable for many experiments. It is commonly collected by displacement of air, or over salt water.

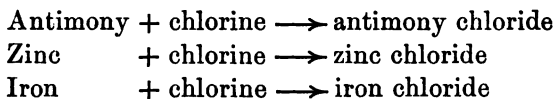
A mixture of salt, sulphuric acid, and manganese dioxide is often used. The salt and sulphuric acid react and form hydrochloric acid, which is then oxidized by the manganese dioxide.

55. Physical Properties. — Chlorine is a greenish yellow gas, nearly $2\frac{1}{2}$ times as dense as air; it dissolves slightly in water; its density and color, however, render its collection by downward displacement a simple matter.

Chlorine has an intensely disagreeable odor, and attacks the membrane of the nasal passages and lungs, producing somewhat the effects of a bad cold. It is very poisonous, a full breath of the pure gas would probably cause death. Inhaling ammonia or alcohol will counteract some of the effects. It should be prepared and handled with caution to prevent its escape.

56. Chemical Properties. — Chlorine is a very active element. It combines directly with many other elements, especially metals, forming chlorides. When powdered antimony is sprinkled into a jar of chlorine, brilliant sparks are seen and a white cloud of antimony chloride is produced. **Action with metals.** Zinc, copper, and iron,

especially when heated, also unite readily with chlorine, with the formation of chlorides.



These are true cases of combustion, since heat and light appear. So we may say chlorine supports combustion, and thus resembles oxygen.

When molten sodium comes in contact with chlorine, it blazes with a dazzling light, sodium chloride (common salt) being formed. To one who for the first time observes the change, it seems almost incredible that a harmless, household necessity like common salt could result from the union of a gas possessing the disagreeable poisonous properties of chlorine, with a metal which has sufficient energy to decompose water.

If a jet of hydrogen is ignited in the air and lowered into a jar of chlorine, the flame will assume a pale white appearance; the color of the chlorine will disappear, and in the jar we will find a colorless gas, hydrogen chloride, which fumes strongly in moist air. Much heat is given off in the union of chlorine with hydrogen, another analogy between chlorine and oxygen. A mixture of chlorine and hydrogen will not combine in the dark; in diffused daylight they combine slowly, and explode when exposed to direct sunlight or other bright light.

The great tendency of chlorine to combine with hydrogen is shown by the fact that it will abstract hydrogen from many compounds. Turpentine is a compound of carbon and hydrogen. If a piece of paper is moistened with warm turpentine and thrown into a jar of chlorine, a

violent action occurs, often with the production of a flame, and a heavy deposit of soot (carbon) forms on the side of the bottle. If the breath is blown into the bottle, the moisture will cause the hydrogen chloride there to fume. An action similar to that with the turpentine is seen in the burning of a wax taper in chlorine. Paraffin wax, like turpentine, contains carbon and hydrogen, and only the latter combines with the chlorine.

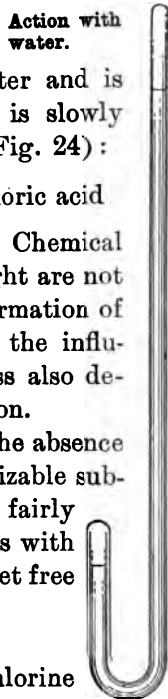
Although water is a very stable substance, under certain circumstances chlorine will react with it, combining with the hydrogen to form hydrochloric acid and setting the oxygen free. If a tube is filled with a solution of chlorine in water and is allowed to stand in the sunlight, oxygen is slowly formed and collects at the top of the tube (Fig. 24):

Water + chlorine \longrightarrow oxygen + hydrochloric acid

The acid formed is dissolved by the water. Chemical actions brought about by the action of light are not uncommon; an important example is the formation of starch in the green leaves of plants under the influence of sunlight. The photographic process also depends on the effect of light on chemical action.

Chlorine is able to decompose water in the absence of light, provided there is present an oxidizable substance. For this reason chlorine water is a fairly good *oxidizing agent*; the chlorine combines with the hydrogen of the water, and the oxygen set free combines with the other material present.

57. Uses. — The chief commercial use of chlorine is as a bleaching agent, especially for cotton goods. Cotton fibre is not naturally *white*. If unbleached or



certain colored goods are placed in a jar of chlorine, no action takes place if the cloth is dry ; but if moist, the

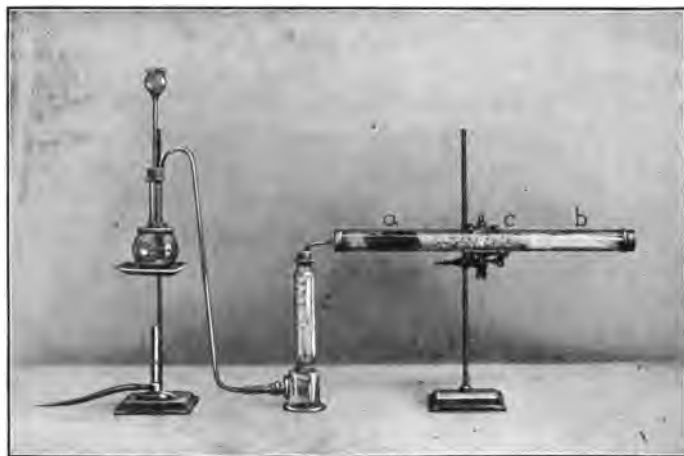


Fig. 25. Bleaching with chlorine.

a, dry colored cloth ; *b*, wet cloth ; *c*, *c*, calcium chloride to keep moisture from dry cloth.

Bleaching. color is quickly destroyed (Fig. 25). Many dyes and the coloring-matter of many fibres are easily oxidizable materials ; so that when the chlorine acts with the water, forming hydrochloric acid, the oxygen set free changes the coloring-matter to colorless compounds. Chlorine will bleach some colored compounds by decomposing them, combining with the hydrogen of the dye.

In bleaching it is not usual to use chlorine gas, but bleaching-powder, a compound obtained by absorbing chlorine in slaked lime. The cotton cloth is soaked in a solution of this, and then in dilute acid to liberate the chlorine, and finally thoroughly washed to remove the chemicals (Fig. 26).

In the bleaching action the destruction of the color was attributed to the oxygen ; but oxygen does not ordinarily

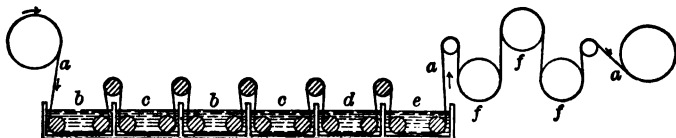


Fig. 26. Diagrammatic representation of bleaching.

a, cloth ; *b, b*, bleaching powder solutions ; *c, c*, acid solutions ; *d*, "anti-chlor" (sodium sulphite solution) ; *e*, water ; *f, f*, drying and ironing rolls.

bleach even weak dyes. It is found that elements in **Nascent state.** general are more active, that is, have a greater tendency to combine with another substance, if they come in contact with it at the moment of liberation. An element acting under these conditions is said to act in the *nascent* (just born) *state*.

Nascent oxygen will readily oxidize and kill microscopic organisms, such as disease germs. Hence chlorine is a **Disinfectant.** good disinfectant. Bleaching-powder (chloride of lime) affords a convenient source of chlorine for this purpose ; on standing exposed to air, chlorine is slowly given off. The gas can be more quickly liberated by the addition of an acid.

Summary.

Chlorine occurs in nature combined with metals, the most important compound being salt.

Chlorine is prepared: (1) by electrolysis of brine; (2) by oxidation of hydrochloric acid; (3) by the action of salt with a mixture of manganese dioxide and sulphuric acid. The first and last methods are the most common.

Atomic weight, 35.5. Density, 3.19 grams per liter. One volume of water at ordinary temperatures dissolves about three volumes of chlorine.

Chlorine is a greenish yellow, poisonous gas characterized by a pungent odor and its chemical activity. It reacts with metals to form chlorides, and with hydrogen and many hydrogen compounds to form hydrogen chloride. Its reaction with water, yielding nascent oxygen, is utilized in bleaching cotton goods.

The principal uses of chlorine are for bleaching and disinfecting.

Exercises.

1. Melted sodium chloride on being electrolyzed gives sodium and chlorine. Why does not the solution yield the same products?
2. In the mixture of salt, sulphuric acid, and manganese dioxide, used in the preparation of chlorine, what is the use of each?
3. If a solution of chlorine is allowed to stand in the sunlight, bubbles collect and the color of the solution fades. Why?
4. Cotton cloth soaked for a long time in chlorine bleaching solution falls to pieces. Why?
5. Chlorine injures wool. What substance, already studied, is used to bleach wool?
6. Describe a case of combustion in which oxygen is not involved.

CHAPTER IX.

HYDROCHLORIC ACID.

58. Preparation. — One of the most important compounds of chlorine is hydrochloric acid, or hydrogen chloride. As its name implies, it may be made by the direct union of hydrogen and chlorine, but the combination is so violent that only small quantities can be made at a time. It may be more conveniently prepared by taking a chloride, *e.g.* sodium chloride, and adding concentrated sulphuric acid (Fig. 27). The action begins immediately and the gaseous hydrogen chloride is evolved so easily that little heating is necessary. Too violent action may be avoided by the successive additions of small quantities of the sulphuric acid to the chloride, using a dropping funnel. The hydrogen chloride gas may be collected by the downward displacement of the air, or, better, over mercury, since this metal is not attacked by the gas. More frequently, however, the gas is dissolved in water and the solution used. The action may be represented thus:

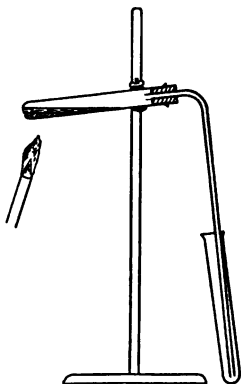
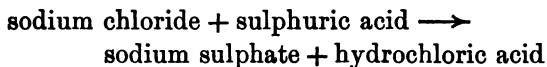


Fig. 27.



The chlorine of the salt combines with the hydrogen from

the sulphuric acid and the sodium with the other part of the sulphuric acid — that is, the part which is not hydrogen.

59. General Method for Preparing Acids. — The preparation of hydrochloric acid illustrates a general method for preparing volatile acids. Sulphuric acid is used because it boils (vaporizes) at a comparatively high temperature (338°C.), while hydrochloric acid vaporizes at a much lower temperature. When the sulphuric acid comes in contact with a chloride, a reaction occurs and some hydrochloric acid is formed. The excess of sulphuric acid and the newly formed hydrochloric acid are then both present in the mixture. The lower boiling hydrochloric acid, however, is soon vaporized, since its boiling-point is many degrees below the temperature at which the operation is conducted. The higher boiling sulphuric acid remains behind and gradually completes its reaction with the sodium chloride. Finally all the hydrochloric acid is driven off and any excess of sulphuric acid remains mixed with the sodium sulphate. The sulphuric acid furnishes the hydrogen for the hydrochloric acid, while chlorine is obtained from the sodium chloride. Sulphuric acid is generally used to prepare acids having a boiling-point lower than 338° .

60. Physical Properties. — Hydrogen chloride is a colorless gas with a sharp, penetrating odor. It is slightly heavier than air.

Its solubility in water is most striking, between four and five hundred volumes of the gas dissolving in one volume of water at the room temperature. This solution, commonly known as hydrochloric acid or muriatic acid, contains about 38% by weight of the hydrogen chloride. The high solubility of the gas causes

Solubility.

it to unite with the moisture of the air, condensation occurs, and the minute particles of the resulting liquid appear as a white mist or fumes which can be seen when a concentrated solution of hydrochloric acid is exposed to the air. The fuming is still more marked when the moist breath is blown across the mouth of a tube from which hydrogen chloride gas is issuing.

Hydrogen chloride can be liquefied and also solidified at low temperatures with increased pressure.

61. Chemical Properties.—Neither liquid hydrogen chloride nor the gas, when perfectly dry, shows the chemical properties characteristic of the acids. These properties belong to the water solution. Hydrochloric acid, then, is the aqueous solution of hydrogen chloride. The water solution has a sour taste, changes blue litmus to red, and reacts with many metals, *e.g.* zinc, iron, or magnesium, setting free hydrogen and forming a compound of the metals which is usually soluble. The equations are:

Zinc + hydrochloric acid \longrightarrow zinc chloride + hydrogen

Iron + hydrochloric acid \longrightarrow iron chloride + hydrogen

In these actions the metal replaces the hydrogen in the acid, forming a *chloride*. Such actions are characteristic of a number of compounds called *acids*. *All acids contain hydrogen which may be replaced by metals.* Substances, like sugar and glycerine, whose hydrogen cannot be replaced by metals, are not classed as acids. In general,

metal + acid \longrightarrow salt of the metal + hydrogen

When an acid reacts with a metal, hydrogen is liberated and is generally evolved as a gas unless there is an oxidizing agent in the solution, in which case the hydrogen may

be oxidized to water. The compound formed by the replacement of the hydrogen of an acid by a metal is called a *salt*. The salt is usually found dissolved in the water which was used to dilute the acid.

The sour taste of acids is an interesting but not an important distinguishing property. Many fruits owe their taste to the presence of acids. Vinegar is hardly more than a dilute solution of acetic acid. The change in color of litmus and of other organic coloring-matters is a convenient way of recognizing acids, but is not reliable in all cases.

Chlorides. Hydrochloric acid, like chlorine, reacts with many metals, forming chlorides.

Metal + hydrochloric acid \longrightarrow metallic chloride + hydrogen
 Metal + chlorine \longrightarrow metallic chloride

All the common chlorides are readily soluble in water except three: silver chloride, mercurous chloride, and lead chloride. *The metals having insoluble chlorides do not react with the acid.*

The insolubility of silver chloride is used as a means of identifying soluble chlorides. If a solution of silver nitrate is added to a solution of a chloride, a white, curdy solid separates; this precipitate darkens in the light.

Chloride of a metal + silver nitrate \longrightarrow
 nitrate of a metal + silver chloride

Addition of silver nitrate causes a white precipitate in many other solutions, but the *silver chloride is insoluble in dilute nitric acid, but dissolves in ammonium hydroxide.* As hydrochloric acid is a solution of *hydrogen chloride*, the same test *together with the litmus test* serves to identify it.

62. Uses. — Very small quantities of hydrochloric acid are found in the gastric juice and are necessary in the gastric digestion. It is often given as a medicine in certain cases of indigestion. Large quantities of hydrochloric acid are employed in the preparation of chlorine to be used in the manufacture of bleaching-powder. It is also used in the making of chlorides, in cleaning metals, and in the manufacture of gelatine.

63. Composition by Volume. — When sodium is placed in hydrogen chloride, a violent reaction occurs, during which the sodium replaces the hydrogen. The reaction can be

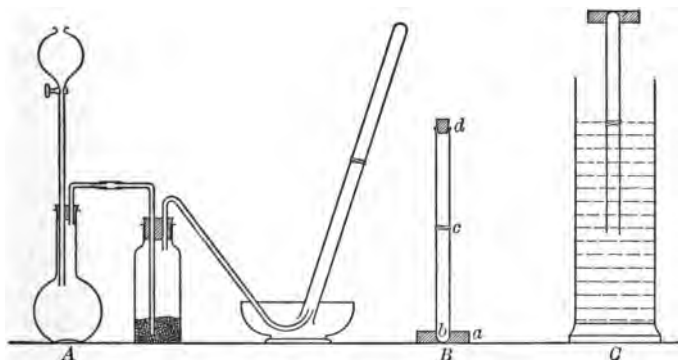


Fig. 28. Volume composition of hydrogen chloride.

a, cork to prevent heating tube while handling; *b*, sodium amalgam; *c*, rubber band; *d*, rubber stopper.

made less energetic by using sodium amalgam instead of sodium. Sodium chloride, mercury, and hydrogen result from the reaction. The volume of the hydrogen remaining after the reaction is found to be one-half that of the hydrogen chloride taken.

Sodium Amalgam Method. — The experiment can be performed in the following manner: hydrogen chloride is

generated by causing sulphuric acid to drop *slowly* into concentrated hydrochloric acid (Fig. 28, *A*). It is then dried by being made to pass through concentrated sulphuric acid. A glass tube, about 70 cm. long and 1.5 cm. in diameter, is filled with the dry hydrogen chloride by the displacement of mercury.

Sodium amalgam is dropped into the tube of hydrogen chloride and the mouth of the tube instantly closed with a stopper (Fig. 28, *B*). The tube is then inverted several times in succession, its mouth placed under some water in a tall cylinder, and the stopper removed (Fig. 28, *C*). Water rushes into the tube.

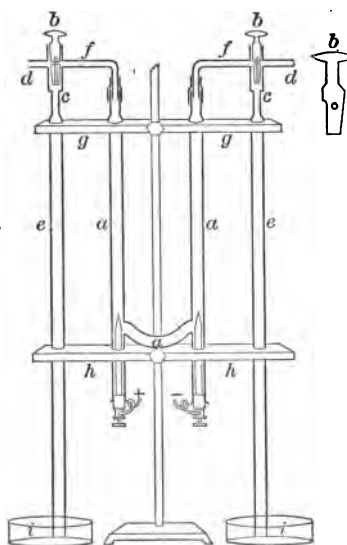


Fig. 29.

Electrolysis of hydrochloric acid.

The remaining gas (hydrogen) is brought under atmospheric pressure by raising or lowering the tube in the cylinder until the liquid on the inside and outside of the tube are at the same level. A small rubber band is then placed on the tube at the surface of the liquid.

The volume occupied by the hydrogen chloride and that occupied by the hydrogen are determined by pouring water into the tube from a graduate to the levels marked by the rubber bands.

Electrolytic Method. — The composition by volume can also be shown by the use of the electrolysis apparatus

shown in Figure 29. Hydrochloric acid, having a specific gravity of 1.1, is placed in the tubes *a*. The three-way stopcocks *b* are turned so that there is a passage from *c* to *d* and a saturated solution of sodium chloride is drawn from the dishes *i* into the collecting tubes *e* until they are filled. The stopcocks are then turned so that there is a passage from *f* to *d*. The current is turned on, and as soon as the hydrochloric acid above the anode is saturated with chlorine, the stopcocks are turned so that the hydrogen and chlorine will pass into the collecting tubes *e*. When the upper surfaces of the sodium chloride solution are just above the support *g*, it is inclined, if need be, so as to mark the relative height of the solution in the collecting tubes. The lower support *h* is then made parallel with *g*. The solution between *g* and *h* is displaced in the same time, showing that equal volumes of hydrogen and chlorine are obtained by the electrolysis of hydrochloric acid.

Summary.

Hydrogen chloride may be prepared: (1) by direct union of its elements; (2) by the action of sulphuric acid with a chloride. The latter is the common method.

It is a gas with a pungent odor. One liter under standard conditions weighs 1.64 grams. One liter of water at 20° dissolves 450 liters of hydrogen chloride.

The dry gas is inactive; its water solution is a typical acid. The replacement of the hydrogen by a metal gives a chloride. All but three of the common chlorides are soluble in water.

Two liters of hydrogen chloride, when decomposed, yield one liter of hydrogen and one liter of chlorine.

The chief uses of hydrochloric acid are for the preparation of chlorine and chlorides, and for cleansing metals.

Exercises.

1. Why is not the direct union of hydrogen and chlorine a practical method of making hydrogen chloride?

2. Acetic acid boils at 118° . Could hydrogen chloride be produced by the action of such acid on sodium chloride?

3. Should hydrogen chloride be collected by upward or downward displacement?

4. Why is tin moistened with a solution containing hydrochloric acid before being soldered?

5. When chlorine is brought in contact with ammonia, which is a compound of hydrogen and nitrogen, a reaction occurs. Name one compound formed.

6. How would you determine whether a gas is hydrogen chloride?

7. What products are formed when metallic magnesium is treated with hydrochloric acid?

8. What is formed when an amalgam of potassium and mercury is exposed to hydrogen chloride?

CHAPTER X.

MOLECULAR COMPOSITION.

- 64. Volume Relations of Gases.** — It has been shown that
1 volume of oxygen with 2 volumes of hydrogen give
2 volumes of steam, and that
1 volume of chlorine with 1 volume of hydrogen give
2 volumes of hydrogen chloride.

The study of the actions of other gases gives similar results; thus:

- 1 volume of nitrogen with 3 volumes of hydrogen give
2 volumes of ammonia.

In these cases the ratio of the volumes of the gases which combine may be expressed in whole numbers; this is also true of the ratio of the volume of each of the combining gases to the volume of the product.

Law of Gay-Lussac. — These relations were first stated by Gay-Lussac in his law of volumes: *The relative combining volumes of gases and the volume of the product, if gaseous, may be expressed by small whole numbers.* Two other generalizations relative to gases are:

Boyle's law: the volume of any gas varies inversely as the pressure; and

Charles' Law: the volume of any gas varies directly as the absolute temperature.

- 65. Reacting Weights and Volume Weights of Gases.** — We found that a volume of chlorine weighs 35.5 times as much as an equal volume of hydrogen if the comparison is made

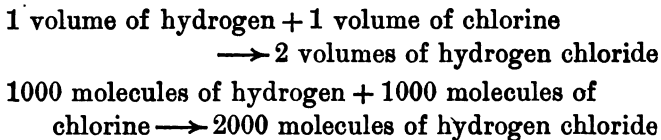
under similar conditions of temperature and pressure. Similarly we found that oxygen weighs 16 times as much as hydrogen. The weights of equal volumes of oxygen and chlorine are, then, as 16 to 35.5. It will be noticed that these numbers are the reacting weights of the elements. A similar regularity is found in the case of other gaseous elements. Hence we make the general statement that *the weights of equal volumes of gaseous elements are to each other as their reacting weights.*

66. Avogadro's Hypothesis.—These uniformities in the behavior of gases were explained by Avogadro in 1811 by the following hypothesis: *Equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.* That is to say, a liter of hydrogen contains just *as many molecules* as a liter of oxygen, a liter of chlorine, a liter of hydrogen chloride, or a liter of any other gas measured under the same conditions of temperature and pressure.

67. Number of Atoms in the Molecules of Gaseous Elements.—In a former chapter (cf. § 51) we showed that if we knew the number of atoms of each element in a molecule, we could determine the relative weight of the atoms. We cannot count the number of atoms in a molecule, but by means of Avogadro's hypothesis we can arrive at a definite *belief* in the matter.

Experiment shows that *one* volume of chlorine and *one* volume of hydrogen combine to form *two* volumes of hydrogen chloride. Suppose the given volume of hydrogen contains 1000 molecules, then by Avogadro's hypothesis, 1000 molecules must also be contained in the volume of chlorine; and, since the hydrogen chloride occupies *twice* the space of the hydrogen, the volume of hydrogen

chloride resulting from the combination must contain 2000 molecules. Or, briefly stated :



In each of these 2000 molecules of hydrogen chloride there must be some hydrogen, at least *one* atom (cf. § 49). At least 2000 atoms of hydrogen have, therefore, been developed from the 1000 molecules ^{Hydrogen} ~~molecules~~ of hydrogen. Consequently, each hydrogen molecule contains *at least two* atoms of hydrogen. Similar reasoning shows that the *chlorine molecule* also contains at least *two atoms*.

It is to be noted that *any even number* might be used instead of two, but since there is no chemical action known in which either the hydrogen or the chlorine molecule seems to divide into more than two parts, it is not probable that there are more than two atoms in either of these molecules.

Let us consider the composition of water. Experiment shows that *two* volumes of hydrogen with *one* volume of oxygen gives *two* volumes of steam. Following the method of reasoning used with hydrogen chloride, *two* molecules of hydrogen plus *one* molecule of ^{Oxygen} ~~molecule~~ oxygen give *two* molecules of steam. There must be at least *one* atom of oxygen in each of the molecules of steam, so the original molecule of oxygen must contain *at least two* atoms. It has been shown that the hydrogen molecule contains at least two atoms. The steam molecule, then, must contain at least one oxygen and two hydrogen atoms.

While the molecules of all the common gaseous elements contain two atoms, this is not true of all elements in the gaseous state. For example, mercury and zinc have each one atom to the molecule; phosphorus has four; and sulphur eight, six, or two according to the temperature.

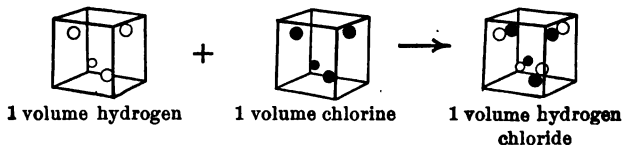
68. Graphic Method of showing Number of Atoms to Molecule.— The following is an *alternative* method for arriving at a belief as to the composition of the molecules of the common gaseous elements.

As all our chemical expressions and calculations are based on the hypothesis of Avogadro, its application merits a fuller study. The number of atoms in the molecules of gases can be demonstrated graphically.

Let us consider the space occupied by four particles of hydrogen, representing the particles by four spheres. A similar space would contain, according to Avogadro's hypothesis, four particles of chlorine. When we say that molecules occupy a given space, we do not mean that they fill that space, but that they occupy it in the sense in which persons are said to occupy a room.



Suppose our volume of hydrogen to unite with the volume of chlorine; if *one* particle of hydrogen combines with *one* particle of chlorine, it is evident that we should have *four* pairs; that is, *four particles*



of hydrogen chloride. These four particles of hydrogen chloride would occupy the same volume as four particles

of hydrogen, or of chlorine, since equal numbers of particles of gases occupy equal spaces. We should then *expect* one volume of hydrogen chloride to be formed.

When one volume of hydrogen actually unites with one volume of chlorine, *two* volumes and not one of hydrogen chloride result. The volume of the acid is twice that of the hydrogen. Each of these two volumes must, according to Avogadro's hypothesis, contain four particles of the acid, or eight in all, so that in the eight particles of the acid there must be *eight* particles of hydrogen and *eight* particles of chlorine.



Each of the original *four* particles must have been composed of *two* smaller particles. The larger particles are *molecules*; the smaller, *atoms*. Therefore, the hydrogen molecules and the chlorine molecules consist each of two atoms.

Summary.

The uniformities in the behavior of all gases, independent of their chemical composition, leads to the belief that equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules. (Avogadro.)

It follows from this assumption, and from the volumetric composition of certain substances, that the elements hydrogen, oxygen, chlorine, and nitrogen have each two atoms to the molecule. Zinc and mercury have one atom to the molecule, phosphorus and arsenic have four.

Exercises.

1. What uniformities (laws) are known about the physical and chemical behavior of gases?

2. What are the evidences in support of Avogadro's hypothesis?

3. The gas carbon monoxide combines readily with oxygen. What relation exists between the volumes of the two gases that will combine with each other?

4. One liter of marsh gas in burning combines with two liters of oxygen. How many molecules of oxygen are needed to react with one molecule of marsh gas?

5. What volume of *air* is needed for the complete combustion of 100 c.c. of marsh gas?

6. About what are the relative numbers of molecules of oxygen and nitrogen in air?

7. Two molecules of nitric oxide (gas) unite with one molecule of oxygen when the two are brought together. How many cubic centimeters of oxygen would be needed for complete reaction with 64 c.c. of nitric oxide? How much air would be needed for the same purpose?

8. Two tanks of equal capacity contain oxygen. The gas in the first is under atmospheric pressure; that in the second is under 3.2 atmospheres' pressure. How does the weight of oxygen in the second tank compare with the weight of that in the first?

9. One volume of hydrogen unites with one volume of bromine gas, forming two volumes of hydrogen bromide. How many atoms are there in the molecule of bromine?

CHAPTER XI.

ATOMIC AND MOLECULAR WEIGHTS.

69. Atomic Weights. — Since it has been shown that there are twice as many hydrogen atoms as oxygen atoms in the molecule of water, the weight of the oxygen atom relative to the weight of the hydrogen atom can now be determined. The oxygen in water weighs eight times as much as the hydrogen. The weight of the *hydrogen atom* is taken as the unit in comparing the weights of the atoms of different elements; therefore, the *two* hydrogen atoms contained in a molecule of water must have a weight of 2. The one oxygen atom combined with the two hydrogen atoms must weigh 8×2 , or 16. The atomic weight of hydrogen is 1; of oxygen, 16. *The atomic weight of an element is a number which expresses how many times its atom is as heavy as the hydrogen atom.*

70. Density and Specific Gravity. — By the density of a substance is meant the number of units of mass which occupy a unit volume. In scientific work the gram is the unit of mass, and the cubic centimeter the unit of volume. The density of a substance, then, is the number of grams of that substance occupying one cubic centimeter. One gram of water at 4° C. occupies one cubic centimeter.

The *specific gravity* of a substance is the weight of that substance divided by the weight of an equal volume of some substance taken as a standard. Water is taken as the standard of specific gravity for liquids and solids.

71. Specific Gravity of Gases. — There are two standards for the specific gravity of gases, air and hydrogen. For experimental purposes air is commonly used; for purposes of calculation hydrogen is more convenient. The specific gravity of a gas with respect to hydrogen is found by determining the weight of a liter of the gas and comparing this weight with the weight of a liter of hydrogen under the same conditions of temperature and pressure. Such comparisons of the weights of equal volumes of gases can be made at any convenient temperature and pressure. The usual custom, however, is to compare weights of equal volumes at 0° C. and 760 mm.; that is, at standard conditions. In the determination of specific gravity, great care must be taken to have the gases pure and dry. Vapor density is another name sometimes used for the specific gravity of gases with respect to hydrogen. The term *density* is often used for specific gravity.

72. Determination of Molecular Weights. — It follows from Avogadro's hypothesis that the weights of equal volumes of two gases will have the same ratio as the weights of their molecules. This can be shown by the following reasoning. One liter of hydrogen, measured under standard conditions, weighs 0.09 gram; one liter of oxygen, measured under similar conditions, weighs 1.43 grams. The liter of oxygen is $\frac{1.43}{0.09}$ or almost 16 times as heavy as a liter of hydrogen. If there are n molecules in a liter of oxygen, there must be, according to Avogadro's hypothesis, n molecules in a liter of hydrogen. Since n molecules of oxygen weigh 16 times as much as n molecules of hydrogen, one molecule of oxygen weighs 16 times as much as one molecule of hydro-

gen. This affords a means of getting the relative weights of the molecules, or what are called *molecular weights*. *The molecular weight of a substance is a number which expresses how many times its molecule is as heavy as the hydrogen atom.* **Molecular weight.**

The hydrogen molecule we showed to contain two atoms, hence its molecular weight is 2. Since a liter of oxygen contains the same number of molecules as a liter of hydrogen, the molecule of oxygen must weigh 16 times as much as the molecule of hydrogen, or 32. Thus we see that the *molecular weight of a gas must be twice its specific gravity referred to hydrogen as a standard*. As chlorine is 35.5 as dense as hydrogen, its molecule weighs 71 times as much as an atom of hydrogen. We have proved that the chlorine molecule contains two atoms, so the atom of chlorine weighs 35.5 times as much as an atom of hydrogen.

73. Alternative Method for Determination of Molecular Weights.¹ —

Since one liter of hydrogen weighs, under standard conditions, 0.09 gram, two grams of hydrogen will occupy $2 \div 0.09$, or 22.22

liters (Fig. 30). The hydrogen molecule we showed to contain two atoms, hence its molecular weight is 2 (cf.



Fig. 30. Gram molecular volume.

¹ The instructor is advised to have class omit either paragraph 72 or paragraph 73. The use of both methods will confuse beginners.

§ 67). There are the same number of molecules in 22.22 liters of any gas (Avogadro's hypothesis). Since the weight of this volume of hydrogen is expressed by a number that is the molecular weight of hydrogen, it follows that *the number expressing the weight in grams of 22.22 liters of any gas will be the molecular weight of that gas.*

22.22 liters of hydrogen weigh 2 grams.

22.22 liters of oxygen weigh 32 grams.

22.22 liters of chlorine weigh 71 grams.

22.22 liters of hydrogen chloride weigh 36.5 grams.

Therefore, 32, 71, and 36.5 are respectively the molecular weights of oxygen, chlorine, and hydrogen chloride.

If 82 c.c. of carbon dioxide weigh 0.1623 gram, we can find the weight of 22.22 liters by the proportion :

$$0.082 : 22.22 :: 0.1623 : x$$

$$x = 44 \text{ grams.}$$

Therefore, the weight of the carbon dioxide molecule is 44. It is 44 times as heavy as the hydrogen atom.

74. Determination of the Number of Atoms in the Molecule of a Compound. — We have shown how the number of atoms in a molecule of a gaseous element is determined in the cases of hydrogen, oxygen, and chlorine (cf. § 67). When the gas is a compound, we can find how many of each kind of atoms are present by ascertaining

(a) the composition by weight;

(b) the molecular weight.

In the case of carbon dioxide:

(a) its composition by weight is 27.3 % carbon, 72.7 % oxygen;

(b) its molecular weight is 44.

The weight of the oxygen in the molecule is 72.7 % of 44, or 32.

We have shown that the *atomic weight* of oxygen is 16, so there must be two atoms of oxygen in each molecule of carbon dioxide.

The carbon in each molecule will be 27.3% of 44, or 12. Carbon cannot be vaporized, consequently we cannot determine its atomic weight by the method used for oxygen. However, many compounds of carbon are gases, and *in no case* does the carbon furnish less than twelve parts of the molecular weight. That is, the smallest portion of carbon that enters into chemical combination (*the atom*) weighs twelve times as much as the hydrogen atom.

The carbon dioxide molecule is composed, therefore, as its name indicates, of *one* atom of carbon (weighing 12) and *two* atoms of oxygen.

Summary.

It follows from Avogadro's hypothesis that the specific gravities of gases are in the same ratio as their molecular weights.

The molecular weight of a gas can be calculated by multiplying the molecular weight of hydrogen, two, by the specific gravity of the gas, hydrogen standard. The specific gravity of a gas is determined experimentally.

The molecular weight of a gas can also be determined by making use of the fact that the molecular weights in grams of all gases have the same volume, 22.22 liters. Knowing the weight of any given volume of the gas, the required molecular weight can be found from a proportion in which the weight and volume and the number 22.22 are the three known quantities.

The molecular weight of hydrogen is 2, of oxygen 32, of chlorine 71, of nitrogen 28.

Problems.

1. A liter of bromine gas, at standard conditions, would weigh 7.2 grams. What is its specific gravity (hydrogen

standard)? Using the answer to question 9, chapter X, determine the atomic weight of bromine.

2. A liter of marsh gas, at standard conditions, weighs 0.72 gram. What is the molecular weight of marsh gas?

3. Methane gas is composed of carbon 75 %, hydrogen 25 %, and its molecular weight is 16. What part of the molecular weight of the compound is carbon? What part is hydrogen? The atomic weight of carbon is 12; how many atoms of each element are there in a molecule of the compound?

4. 0.58 gram of acetylene gas has a volume of 495.7 c.c., standard conditions. What is the specific gravity of acetylene? What is its molecular weight?

5. Determine the molecular weight of the following substances:

GAS.	WEIGHT DATA.
Nitrous oxide.	290 c.c. weighs 0.574 g.
Hydriodic acid	93 c.c. weighs 0.531 g.
Ether (gaseous conditions)	230 c.c. weighs 0.766 g.

6. Air is 14.44 times as heavy as hydrogen. Compute the specific gravity, air standard, of the gases mentioned in the above problems.

7. What is the numerical ratio between the molecular weight of a gas and its specific gravity, hydrogen standard? What is the ratio between the molecular weight and the specific gravity, air standard?

8. Determine the molecular weights of the following gases:

GAS.	SP. G. (AIR).
Ammonia	0.597
Carbon monoxide	0.968
Cyanogen	1.806

CHAPTER XII.

SYMBOLS AND FORMULAS.

75. It is a great convenience to have a short, accurate method of representing the ch  mical changes taking place in a chemical action. We have been expressing those changes in the form of equations, in which we have on one side the names of the substances which enter into the action, and on the other the names of the products formed. According to the atomic theory, chemical action takes place between molecules, by the rearrangement and redistribution of the atoms. If we express the action in terms of molecules and atoms, it becomes much more significant. Symbols are used to represent chemical action as simply as possible.

76. **Significance of the Symbol.** — The symbol of an element is usually the initial letter of the name capitalized. Thus H means *one atom* of hydrogen, and as the atom has mass, it represents also a *definite mass* of hydrogen, *one part by weight*. The symbol thus means not only the substance but a definite quantity of the substance. O means one atom of oxygen, *also* sixteen parts by weight of oxygen.

When several substances have the same initial, another letter conspicuous in the name is added, but not capitalized, as C (carbon); Ca (calcium); Cd (cadmium); Cl (chlorine). In some cases the symbol is derived from the Latin name, as Fe (*ferrum*, iron); Cu (*cuprum*, cop-

per); Na (*natrium*, sodium); and K (*kalium*, potassium).

77. Significance of the Formula. — The formula of a molecule is formed by grouping together the symbols of the atoms composing it. The molecule of hydrochloric acid was found to consist of one atom of hydrogen and one atom of chlorine. Its formula, therefore, is HCl. This means

- (1) one molecule of hydrochloric acid;
- (2) one molecule of hydrochloric acid containing one atom of hydrogen and one atom of chlorine;
- (3) one molecule of hydrochloric acid composed of 1 part by weight of hydrogen and 35.5 parts by weight of chlorine;
- (4) 36.5 parts of hydrochloric acid by weight;
- (5) 1 part by volume of hydrochloric acid (Avogadro's hypothesis).

When a molecule contains more than one atom of the same kind, the symbol is not usually repeated, but the number of the atoms is written as a subscript to the symbol. The formula of water is usually written H_2O and not HOH. As stated above, H_2O means

- (1) one molecule of water;
- (2) one molecule of water composed of two atoms of hydrogen and one atom of oxygen;
- (3) one molecule of water composed of 2 parts by weight of hydrogen and 16 parts by weight of oxygen;
- (4) 18 parts by weight of water;
- (5) 1 part by volume of steam.

In many cases the molecular weight of a substance can be determined only indirectly; in other cases it cannot be determined at all. In these cases the formula expresses the simplest combination that will agree with the percentage composition. Thus, NaCl represents one molecule of sodium chloride as composed of one atom of sodium and one atom of chlorine; that is, 23 parts by weight sodium and 35.5 parts chlorine, or a total weight of 58.5 sodium chloride. It also represents one volume of the *gaseous salt*, but *not* of the *solid*.

The number of molecules which take part in a reaction is represented by means of coefficients.

$2 \text{HCl} = 2$ molecules hydrochloric acid

$3 \text{H}_2\text{O} = 3$ molecules water

78. Calculation of the Percentage Composition from the Formula. — If the formula of a compound is known, and also the atomic weights of the elements composing it, the percentage composition can be calculated. Thus the formula of an iron oxide is Fe_2O_3 ; the atomic weight of iron is 56, of oxygen 16.

The formula represents:

2×56 , or 112 parts by weight of iron, and

3×16 , or 48 parts by weight of oxygen, making

160 parts by weight of iron oxide.

$\frac{112}{160}$, or 70 per cent by weight is iron, and

$\frac{48}{160}$, or 30 per cent by weight is oxygen.

79. Calculation of the Formula from the Percentage Composition. — If we know the percentage composition and the atomic weights, we can calculate the formula. Thus, alcohol is composed of: carbon, 52.17%; hydrogen,

13.04%; oxygen, 34.78%. Dividing each of these by the weight of one atom of the element, we get:

$$\text{Carbon} \quad \frac{52.17}{12} = 4.34;$$

$$\text{Hydrogen} \quad \frac{13.04}{1} = 13.04;$$

$$\text{Oxygen} \quad \frac{34.78}{16} = 2.17.$$

The numbers 4.34, 13.04, and 2.17 bear the same relation to each other as do the respective number of carbon, hydrogen, and oxygen atoms in a molecule of the compound. Since, however, atoms are indivisible, the numbers expressing them must be whole numbers. To reduce the numbers in this case to integers, divide each by 2.17, the smallest number, viz.:

$$\text{Carbon} \quad \frac{4.34}{2.17} = 2;$$

$$\text{Hydrogen} \quad \frac{13.04}{2.17} = 6;$$

$$\text{Oxygen} \quad \frac{2.17}{2.17} = 1.$$

The simplest formula, based on these relative numbers of atoms, is $\text{C}_2\text{H}_6\text{O}$. This requires a whole molecular weight of

$$(2 \times 12) + (6 \times 1) + (1 \times 16) = 46.$$

The specific gravity of alcohol vapor referred to hydrogen is found to be 23, which *requires* a molecular weight of 46 (cf. § 72); the molecular weight calculated from the simplest formula agrees with this. Therefore, $\text{C}_2\text{H}_6\text{O}$ is not only the simplest but the *correct* formula for a molecule of alcohol.

For acetylene:

	percentage by weight.		atomic weight.		atomic ratio.	simplest atomic ratio.
Carbon	92.30	+	12	=	7.69	1
Hydrogen	7.69	+	1	=	7.69	1

The simplest formula agreeing with the analysis would be CH ; this requires a molecular weight of $(12 + 1)$, 13. The specific gravity is found to be 13, so that the molecular weight must be 26 (cf. § 72), and the formula of the molecule must be C_2H_2 .

For sulphuric acid:

	percentage by weight.		atomic weight.		atomic ratio.	simplest atomic ratio.
Hydrogen	2.041	+	1	=	2.04	2
Sulphur	32.653	+	32	=	1.02	1
Oxygen	65.306	+	16	=	4.08	4

The simplest formula agreeing with this composition is H_2SO_4 .

Problems.

1. State the meaning of every symbol and figure in each of the following formulas:

HCl
 H_2SO_4
 5CO_2
 $\text{Ca}(\text{NO}_3)_2$
 $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

2. How many atoms of hydrogen in each of the following?

HBr
 H_2SO_3
 NH_3
 $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
 $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$

3. Making use of the table of atomic weights in the Appendix, calculate the molecular weights of the following compounds:



4. Determine the specific gravity (hydrogen standard) of each of the following gases:



5. Calculate the weight of a liter of each of the following gases:



6. Acetylene gas has the formula C_2H_2 . What is the weight of a liter of it?

7. What per cent of potassium chlorate, KClO_3 , is oxygen?

8. If a sample of washing soda has a composition represented by the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, what per cent of it is water?

9. A hundred grams of a compound contain 30.43 grams of nitrogen and 69.57 grams of oxygen. What per cent of the compound is nitrogen and what per cent is oxygen? What is the ratio between the number of nitrogen atoms and the number of oxygen atoms? What is the simplest formula that could be used to express the composition of the compound?

10. Calculate the percentage composition of the compound whose molecule is represented by the formula $\text{Ca}(\text{NO}_3)_2$.

11. A substance on analysis was found to contain carbon 40 %, hydrogen 6.67 %, and oxygen 53.33 %. What is the simplest formula that could be used to represent such a substance?

12. Calculate the empirical (simplest) formula of a compound containing calcium 29.41 %, oxygen 47.06 %, and sulphur 23.53 %.

13. The specific gravity of a certain gas, hydrogen standard, is 14. What is the molecular weight of the gas? It is composed of carbon 42.8 % and oxygen 57.1 %. What is its formula?

14. Alcohol, a liquid at ordinary temperatures, is readily converted into a gas; 0.247 gram of the gas has a volume of 184.9 c.c. at a temperature of 150°C . What is the specific gravity of the gas, hydrogen standard? What is the molecular weight of alcohol? Alcohol is composed of carbon 52.2 %, hydrogen 13.0 %, oxygen 34.8 %. Determine its formula.

15. 0.55 gram of a certain gas has a volume of 277.7 c.c. at standard conditions. The gas is composed of nitrogen 63.6 %, oxygen 36.3 %. What is the formula of the substance? (At. wt. N = 14.)

16. 0.35 gram of a liquid that is easily vaporized has, in the gaseous form, a volume of 99.7 c.c. (corrected). The substance is composed of carbon 92.3 %, hydrogen 7.7 %. Determine the formula of the substance.

CHAPTER XIII.

CHEMICAL EQUATIONS.

80. Chemical Reactions Represented by Equations. — Since the symbol of an element and the formula of a compound represent more than the name, we may use them instead of the names in the equations we have employed, and then the equation will represent definite numbers and masses as taking part in the reaction. The reacting substances are usually written first, on the left; the products on the right; the arrow (or the equality sign) is not to be read as "equal to," but as *give* or *form*; the addition sign, as *with*. As the change may occur under different conditions, no attempt is made to represent *how* the action occurred.

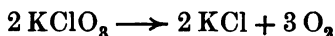
These equations are not algebraic; they cannot be calculated or predicted with certainty. They represent changes which actually take place. When we know by experiment:

- (1) that substances will react;
- (2) the composition of each substance;
- (3) all the products formed;
- (4) the composition of each product;

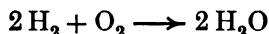
we can represent the reaction by an equation, and calculate the relative quantities involved.

The fundamental principle upon which chemical calculations depend is the indestructibility of matter, so the equation must represent the same amount of each element after the change as before. There must be the same

number of atoms of each element represented on each side of the equation. On heating potassium chlorate, only two products result, potassium chloride and oxygen. Potassium chlorate has the composition shown by the formula KClO_3 ; potassium chloride, KCl ; and we have shown (page 75) that there are two atoms in the molecule of oxygen, O_2 . Using these formulas, we have: $\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$; but it will be seen that there are three atoms of oxygen on the left and only two on the right-hand side of the equation. In order that the quantities and compositions shall be correctly represented, the equation must be written :

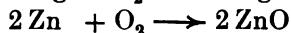
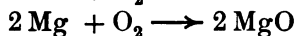
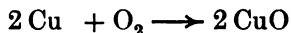


In this equation the number of atoms of each element is the same on the two sides of the equation. So, also, we must write :

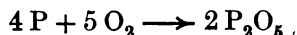


Materials which are present, but which undergo no change, such as water in which the substances are dissolved, catalytic agents, etc., are not expressed in the equation.

81. Equations for Reactions Already Studied. — The heating of copper, magnesium, and zinc in the air result in the formation of the oxide of the metal heated in each case. The equations are :

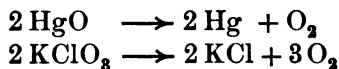


The slow oxidation of phosphorus, made use of in the analysis of air, and the burning of phosphorus in oxygen are both represented by the equation :

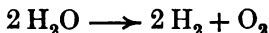


Thus we find that the product, phosphorus pentoxide, is the same whether the phosphorus combines with the oxygen slowly and quietly, or rapidly and violently. All the above equations illustrate the process of direct combination or *synthesis*.

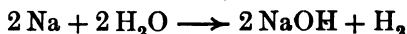
The production of oxygen from mercuric oxide and from potassium chlorate illustrates the opposite process, decomposition or *analysis*. The equations are:



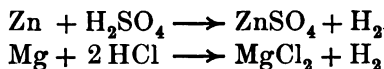
82. The equation for the *preparation of hydrogen* by electrolysis of water is:



When sodium reacts on water, we have:

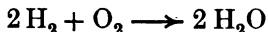


For the formation of hydrogen by the reaction between metals and acids, we have the following equations:



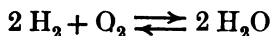
The formulas of sulphuric acid and zinc sulphate show very clearly how the latter is produced by the replacement of the hydrogen of the acid by the zinc. The formation of sodium hydroxide and magnesium chloride in the equations given above furnish other examples of *replacement*.

83. The *formation of water* by the burning of hydrogen in oxygen or in air is represented by the equation:

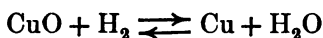


It will be noticed that this is the exact reverse of the equation given above for the decomposition of water;

a large proportion of our equations are *reversible*; the direction in which the reaction proceeds depends upon the conditions. This may be shown by the use of the double arrow; so we may write the equation:

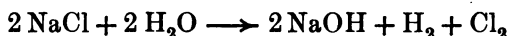


The reduction of copper oxide by hydrogen is expressed by the equation:



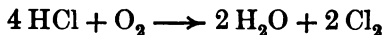
This equation is reversed with the liberation of hydrogen, when steam is passed over heated copper.

84. The equation for the *preparation of chlorine* by electrolysis of brine is:

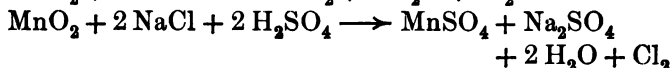


The equation represents the final result of the reaction, and does not show the intermediate steps; viz. the separation of the sodium and chlorine, and the reaction of the sodium with the water.

The liberation of chlorine by the oxidation of hydrochloric acid in the presence of a catalytic agent is represented by the equation:



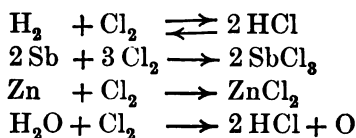
When manganese dioxide is used as the oxidizing agent, the equations are:



A comparison of these three equations shows the formation of water and chlorine in each case. We shall see

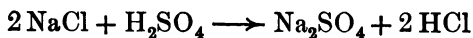
from the equation for the formation of hydrochloric acid given below, that in all three methods we may regard the liberation of the chlorine as the result of the oxidation of the hydrogen of hydrochloric acid.

85. The following equations represent the reaction of chlorine with various substances, resulting in the *formation of chlorides*:



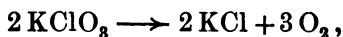
The last equation represents the liberation of nascent oxygen, in the bleaching by chlorine, so we write the symbol O, indicating the oxygen atom, and not O₂, indicating the oxygen molecule. It will be seen that this equation is the reverse of that given above for the preparation of chlorine.

86. Two methods for producing *hydrochloric acid* are indicated in the equations just given. We may represent its formation from salt and sulphuric acid as follows:



This equation illustrates *double replacement*, or, as it is more often called, double decomposition; each compound apparently breaks up into two parts, each of which unites with a different part of the other compound. Such reactions can only be prevented from becoming reversible by the removal of one of the products from the field of action; in this case hydrochloric acid is driven off as a gas. Double replacements are common in solutions.

87. Calculation of Relative Weights from the Equation. —
In the equation



the molecule of potassium chlorate weighs

$$39 + 35.5 + 3 \times 16 (122.5);$$

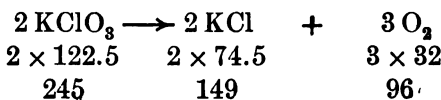
the molecule of potassium chloride weighs

$$39 + 35.5 (74.5);$$

the oxygen molecule weighs

$$2 \times 16 (32).$$

That is, 2×122.5 , or 245 parts by weight of potassium chlorate, on being decomposed, give 2×74.5 (149) parts of potassium chloride; and 3×32 (96) parts of oxygen.



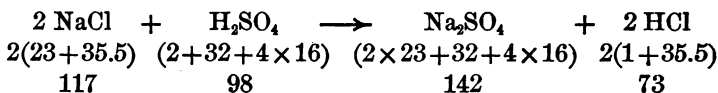
Suppose we wish to prepare 20 grams of oxygen; how much potassium chlorate must be used? From the numbers we find that for every 96 parts of oxygen produced, 245 parts of potassium chlorate were used; so we may obtain the number sought for from the proportion:

$$96 : 245 :: 20 \text{ grams} : x$$

$$96x = 4900.$$

$$x = 51.0 \text{ grams, the potassium chlorate needed.}$$

What quantity of sulphuric acid (H_2SO_4) is needed to exactly decompose 100 grams of sodium chloride, when sodium sulphate and hydrochloric acid are formed?



The weight of the sodium chloride decomposed and the weight of the sulphuric acid needed will be as 117:98. Forming the proportion:

$$\begin{aligned}
 117:98::100 \text{ grams}:x \\
 x = 83.7 \text{ grams, sulphuric acid required.}
 \end{aligned}$$

Similarly the weights of the sodium sulphate and of the hydrochloric acid might be found:
for the sodium sulphate,

$$117:142::100 \text{ grams}:x$$

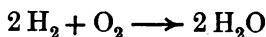
for the hydrochloric acid,

$$117:73::100 \text{ grams}:x$$

In any reaction the weights of the molecules involved have the same ratio as the weights of the reacting substances. We have used this relation in the calculations above.

88. Calculation of Volume Relations and Volumes from the Equation.—What has been said in the preceding paragraphs applies to all substances, solid, liquid, or gaseous. But in the case of gases, we found the formula has a meaning that did not apply to liquids or solids (cf. § 77).

In the equation:



it appears that two molecules of hydrogen react with one molecule of oxygen to form two molecules of steam. Since equal numbers of molecules occupy equal volumes, the volume of the hydrogen must be twice that of the oxygen and equal to that of steam.

In the equation :



we see that *two molecules* of chlorine are used to liberate one molecule of oxygen, hence two volumes of chlorine will furnish one volume of oxygen. Therefore, *in the case of gases*, the coefficients represent the *relative volumes of the substances*.

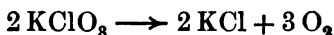
The equation



may be read: 1 part by volume of hydrogen with 1 part by volume of chlorine will give 2 parts by volume of hydrochloric acid; and also 2 parts by weight of hydrogen and 71 parts by weight of chlorine give 73 parts by weight of hydrochloric acid.

Moreover, since the molecular weight in grams (gram molecular weight) of any gas has a volume of 22.22 liters at standard conditions, the volumes of gases reacting can be directly calculated from the equation.

In the decomposition of potassium chlorate:

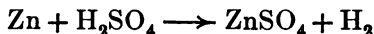


only one of the substances is gaseous; 245 grams of potassium chlorate give 3 gram molecules of oxygen (3O_2), which occupy 3×22.22 liters. If we wish to produce 100 liters of oxygen, we can find the weight of potassium chlorate needed, by the following proportion :

$$66.66 \text{ liters} : 100 \text{ liters} :: 245 \text{ grams} : x$$

$$x = 367.5 \text{ grams, potassium chlorate needed.}$$

If we wish to produce 50 liters of hydrogen by the reaction



65 grams of zinc give one gram molecule of hydrogen (22.22 liters), therefore :

$$22.22 : 50 :: 65 \text{ grams} : x$$

$$x = 146.2 \text{ grams, zinc needed.}$$

Summary.

Chemical reactions are represented by equations in which the reacting substances are written on the left and the products on the right, separated by an equality sign or an arrow.

Equations represent actual chemical changes and must indicate the same amount of each element after the change as before. The composition of each reacting substance and of all the products must be known before the equations can be written. Solvents which are unaffected and catalytic agents are not expressed in the equation. The conditions of the chemical action are not indicated by the equation.

Equations may represent processes of :

- (a) direct combination;
- (b) decomposition;
- (c) simple replacement;
- (d) double replacement;
- (e) oxidation and reduction.

The *relative weights* of the different substances in a chemical equation can be calculated. Such calculations deal with *but two* of the substances at a time. The weights of the substances are in the same ratio as the weights of the molecules involved. With the weight in grams of one of the substances known, and the weights of the molecules ascertained, a proportion is formed with ~~these three~~ quantities. The weight in grams of the second substance is found by solving the proportion.

Coefficients of molecules of gaseous substances, as expressed in an equation, represent relative volumes. The *gram molecular weight* of any gas occupies 22.22 liters at standard conditions. By making use of these two facts, the volumes of gases as well as their weight can be calculated from chemical equations.

Exercises.

1. Write an equation for (a) a synthesis, (b) an analysis.
2. Write the equation for what takes place when potassium, a metal similar to sodium, reacts with water. What process does the equation represent?
3. Write a reversible equation involving hydrogen and chlorine. Tell how you can control the direction in which the action proceeds.
4. Write the equation for the reaction that might be reasonably expected to occur if sodium chlorate, NaClO_3 , is heated.
5. Write the equations for the reaction of potassium chloride, KCl , with sulphuric acid. Name the process and the products. Explain why the reaction is not ordinarily reversible.
6. Write the equation for a laboratory preparation of chlorine.
7. Write the equation expressing the reaction of magnesium with oxygen; with sulphuric acid; with chlorine; and with hydrochloric acid.
Name the products and the process illustrated in each case.
8. Calculate the weight of oxygen obtained from heating 20 grams of mercury oxide.
9. How many grams of copper were heated to form 2.64 grams of copper oxide?

10. 2.4 grams of zinc were treated with an excess of dilute sulphuric acid. Calculate weight of each product formed.

11. Find how many grams (a) of potassium chloride, KCl, and (b) of sulphuric acid are needed to produce 2.8 grams of hydrogen chloride.

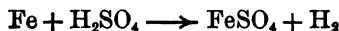
12. Calculate the weight of manganese dioxide and that of hydrogen chloride used to produce 4.8 grams of chlorine. How many grams of manganese chloride were formed?

13. How many liters of oxygen at standard conditions can be obtained by heating 8.4 grams of potassium chlorate?

14. State the relative volumes of each gaseous substance indicated by the equations representing:

- (a) hydrogen combining with chlorine;
- (b) chlorine combining with water;
- (c) hydrogen combining with bromine;
- (d) electrolysis of sodium chloride.

15. How many kilograms of iron would be required to furnish hydrogen enough to fill a balloon of 6350 cubic meters capacity?



CHAPTER XIV.

SODIUM AND POTASSIUM.

89. Preparation of Sodium. — The great chemical activity of sodium and the stability of its compounds made the preparation of metallic sodium a difficult chemical problem. Like many others, it has been solved by the application of electricity. Sir Humphry Davy, in 1807, obtained both sodium and potassium by the electrolysis of the melted hydroxides, and the metals are now prepared commercially by this method (Fig. 31).

When the current is passed through the melted hydroxide, the sodium and hydrogen appear at the cathode and the oxygen at the anode. The hydroxide is contained in an iron cylinder and melted by gas flames beneath. The cathode is a carbon cylinder coming up through the bottom. The anode is an iron or nickel cylinder coming down from the top and surrounding the cathode. Between the electrodes is suspended a cylinder of wire gauze (*c, c*) through which the fused hydroxide (*a*) can pass, but which prevents the passage of bubbles of the gas or globules of melted so-

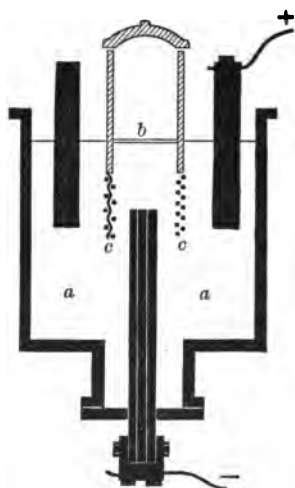


Fig. 31.

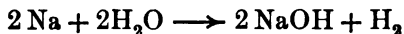
dium. The sodium, being lighter than the hydroxide, rises to the surface (*b*) above the cathode, and is ladled off from time to time. The hydrogen escapes through holes in the cover and the oxygen is led off through a pipe from the side. The reasons for these precautions will be readily understood when we keep in mind the energy with which oxygen combines with both sodium and hydrogen. The heat generated by the passage of the current is sufficient to keep the hydroxide molten after the action starts.

90. Physical Properties of Sodium. — Sodium is a silver-white metal, possessing a brilliant lustre when in a pure state. It is soft enough at ordinary temperatures to be readily cut with a knife and to be moulded by the fingers. It may be formed into wire by pressing it through a hole in a metal plate. It is a good conductor of heat and electricity; silver, copper, and gold are the only metals that surpass it in this respect. "Metallic" lustre and conductivity are characteristic physical properties of metals. It is a very light metal, slightly less dense than water.

91. Chemical Properties of Sodium. — Sodium is in general a very active element chemically. It burns readily in oxygen and in chlorine, and is an energetic reducing agent. The color of its flame is bright yellow, and this color is imparted to a non-luminous flame when any sodium compound is heated in it.

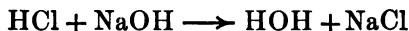
The most striking chemical property of sodium is its action in water. Exposed to moist air, it tarnishes almost instantly, on account of the formation of a layer of sodium hydroxide. In perfectly dry air it remains unchanged at ordinary temperatures.

When thrown on water, it skims over the surface with a hissing sound. The water is rapidly decomposed, one-half the hydrogen being set free and the sodium combining with the oxygen and the other half of the hydrogen to form sodium hydroxide:



The hydroxide dissolves in water and may be obtained by evaporation. A large amount of energy is liberated in the decomposition of water by sodium, which may be readily shown by dropping a piece of sodium on a moist piece of filter paper. In this way the heat is all liberated at one place and is sufficient to ignite the hydrogen. On account of its ready action with water, the sodium is always kept under kerosene or some other oil containing no oxygen.

92. Sodium Hydroxide as a Typical Base. — A solution of sodium hydroxide turns red litmus blue, an action exactly the reverse of that of an acid. If we mix solutions containing weights of hydrochloric acid and sodium hydroxide proportional to their molecular weights, there is a rise of temperature, and the resulting solution affects neither red nor blue litmus. This solution contains sodium chloride, a fact which is clearly indicated by its taste. As the acid and the hydroxide have both lost their characteristic properties, the resulting solution is said to be *neutral* and the process is known as *neutralization*. The change may be expressed by the equation:



A compound whose solution turns red litmus blue and neutralizes acids is called a *base*. Sodium hydroxide, then, is a typical base.

93. Spectrum Analysis.—The colors imparted to flames by different elements furnish a simple and valuable method of analysis. The different colors found in light are bent to different degrees in passing through a prism, and are so separated from each other. The band of light thus produced is known as a *spectrum*, and the instrument used to produce and view the spectrum is called a *spectroscope*. The light to be studied is admitted through a narrow slit (*A*) in the end of a tube, in such a way that it will fall in parallel rays on a prism (*C*) with its edges parallel to the slit. When the beam emerges from the prism, the different colors are separated and the spectrum is viewed through lenses (*E*) placed at the end of another tube (Fig. 32).

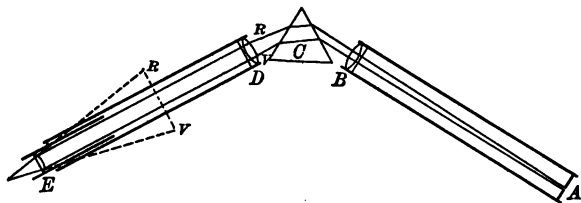


Fig. 32. Diagrammatic representation of spectroscope.

White light, produced by an incandescent solid, gives a spectrum consisting of a continuous band of color, shading from red through orange, yellow, green, blue, and indigo to violet. When the light is due to incandescent vapors, the spectrum consists of a series of bright lines, the color and position of which differ for each element. The yellow color spoken of above is due to the presence of sodium vapor in the flame. This may be most conveniently produced by placing in a flame a platinum wire moistened in a solution of a sodium compound. Such a

flame when viewed with a spectroscope shows two yellow lines very close together. The spectrum of potassium consists of a double line in the violet end and a line in the red end of the spectrum. Lithium is a rare metal closely related to sodium and potassium. It was thought to exist in very few minerals until the spectroscope showed that small quantities of it were widely distributed throughout nature. Its spectrum consists of a bright red line and a very faint yellow line. The presence of one-millionth of a milligram of lithium can be shown by means of the spectroscope. (For spectra of some familiar elements, see Fig. 33, frontispiece.)

94. Potassium and its Preparation. — Potassium resembles sodium in so many respects that it may be very briefly discussed.

Its preparation is similar to that of sodium, substituting potassium hydroxide for sodium hydroxide.

95. Properties of Potassium. — Potassium is a very silvery white metal with a slight bluish tinge. It is softer than sodium, lighter, and melts at a lower temperature. Although sodium and potassium are solids at ordinary temperatures, an alloy of the two can be prepared which is a liquid.

The chemical properties of potassium closely resemble those of sodium, but it is more active. It decomposes water, forming potassium hydroxide and liberating hydrogen. The energy produced is sufficient to ignite the hydrogen, as the potassium skims over the surface (Fig. 13, page 27). Potassium imparts a reddish violet color to the flame. As the presence of a slight trace of sodium obscures the potassium flame, several thicknesses of cobalt

blue glass should be interposed between the flame and the eye to absorb the yellow sodium light.

Summary.

	ATOMIC WT.	SPECIFIC GR.	MELTING PT.	BOILING PT.
Sodium	23.0	.97	97.6°	877°
Potassium	39.1	.87	62.5°	757°

Both *metals* are soft and light. They react with water to form the hydroxides, and with acids to form salts.

Their *compounds* are characterized by the colors they impart to a non-luminous flame. Most of the compounds are colorless (white when powdered), and soluble in water, the potassium compounds being more soluble.

The hydroxides are typical bases — caustic, alkaline, and neutralizing acids. They are used in the preparation of soaps and bleaching solutions, in oil-refining, and in glass-making.

Exercises.

1. Compare the properties of sodium with the corresponding properties of metals with which you are more familiar, for example, iron, copper, silver. Do you find any resemblances?
2. Why is sodium classed as a metal?
3. What are the most essential properties of metals from the chemical point of view?
4. Calculate the quantity of sodium that could be obtained from 1 kilogram of pure sodium hydroxide.
5. Calculate the quantity of sodium hydroxide that would be formed by the action of 5 grams of sodium on water. What weight of hydrogen would be evolved? What volume would the hydrogen have under standard conditions?
6. What weight of hydrogen chloride would be required for the complete neutralization of 2.63 grams of sodium hydroxide?

CHAPTER XV.

SOLUTION.

Solutions have already been defined (chapter VI) and some of their properties discussed. We have found that many of the reactions studied take place only in the presence of water, even though the water itself does not react. The purpose of the present chapter is to furnish an explanation of these various phenomena.

96. Electrolytes and Non-electrolytes. — Solutions differ from each other greatly in their power to conduct electricity. We have already seen that water solutions of sodium chloride and sulphuric acid (electrolysis of water)

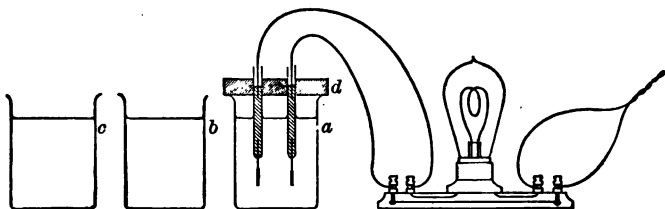


Fig. 34. Determination of electrolytes.

a, b, c, beakers containing solutions to be tested; *d*, cork carrying electrodes with mercury contacts.

readily permit the passage of the current. We may test other solutions by arranging the following circuit, including a source of current, the substance to be tested, and some instrument to detect the passage of the current (Fig. 34).

The incandescent lamp serves two purposes. Its resistance cuts down the current to a strength suitable for passing through a solution. Secondly, if the lamp lights, the current must be passing through the liquid in the circuit, and the solution is a conductor. The brilliancy with which the lamp glows roughly indicates how well the solution in the circuit conducts.

When distilled water is put into the circuit, the lamp does not even glow ; hence, in those water solutions which are conductors the current must be carried by the aid of the dissolved substance. A solution of hydrochloric acid conducts the current readily ; a water solution of sugar fails to conduct, but sodium hydroxide, a typical base, proves as good a conductor as hydrochloric acid. Solutions of sulphuric acid, potassium hydroxide, sodium chloride, sodium sulphate, and copper sulphate all allow the lamp to glow brilliantly. Glycerine, alcohol, and many similar compounds are found to be non-conductors.

Our circuit includes two different classes of conductors. The first consists of solid conductors, chiefly metallic, **Classes of** such as the copper wire and the carbon filament **conductors.** of the lamp. These conductors undergo no permanent change in carrying the current. The other class includes those liquids which we have found to be conductors, the components of which are free to move toward the electrodes, which are the points where the current enters and leaves the liquid. In these liquid conductors the transmission of electricity is attended by the decomposition of the conductors, components of which may be liberated at the electrodes. A liquid which is decomposed during the passage of an electric current is called an *electrolyte*. The name given to the process is *electrolysis*.

Arranging the electrolytes and non-electrolytes in two columns, we have

ELECTROLYTES	NON-ELECTROLYTES
hydrochloric acid	distilled water
sulphuric acid	
sodium hydroxide	sugar
potassium hydroxide	
sodium chloride	glycerine
sodium sulphate	
copper sulphate	alcohol

An examination of the column of electrolytes shows that it contains only acids, bases, and salts. All electrolytes belong to these classes of compounds. The non-electrolytes in the second column are not generally placed in any of these classes of compounds. Why is it that water solutions of acids, bases, and salts conduct electricity, while other substances fail? This question has led to a more careful study of the properties of water solutions.

97. Effect of Dissolved Solids on the Freezing-point. — Under ordinary conditions of pressure pure water freezes at 0° C. and boils at 100° C. The addition of any soluble solid lowers the freezing-point and raises the boiling-point. We shall discuss only the freezing-point. All water solutions freeze at a lower temperature than pure water. Careful measurements show that the amount of the lowering depends on the mass of the substance added. A solution containing 10 grams of sugar to one liter of water will freeze at a point twice as far below 0° as one containing 5 grams of sugar to 1 liter of water. According to the atomic theory 10 grams of sugar contain twice as many molecules as 5 grams. Therefore, the

lowering of the freezing-point of the pure solvent is proportional to the number of sugar molecules dissolved.

The depression of the freezing-point of water (Fig. 35)¹ produced by equal numbers of molecules of different substances has been carefully determined. To get equal numbers of molecules, a weight in grams equal to the molecular weight of each substance was dissolved in one liter of water. Thus 46 grams of alcohol, C_2H_5OH , and 342 grams of sugar, $C_{12}H_{22}O_{11}$, were dissolved in a liter of water. In both cases the resulting solutions freeze at -1.86° . It was further found that a solution of any non-electrolyte containing the molecular weight in grams of the solute to the liter gave this same lowering of the freezing-point. If weights of non-electrolytes proportional to their molecular weights are dissolved in equal volumes of the same solvent, the solutions will freeze at the same temperature. This is strictly true for dilute solutions only. This indicates that the depression of the freezing-point is dependent on the *number* of molecules present

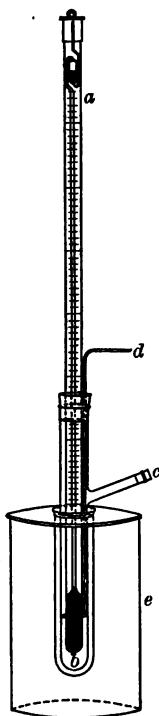


Fig. 35.

and not on the weight or kind of these molecules. But if common salt is used, we find that, in dilute solution, the

¹ Figure 35 represents an apparatus for determining the depression of the freezing-point. A Beckmann thermometer (a) is used and the liquid to be frozen is held in the inner tube (b). Through the side tube (c) is introduced the substance whose effect on the freezing-point of the pure solvent is to be determined. A stirring rod (d) moves up and down in the solution which is cooled by a freezing mixture contained in the outer vessel (e).

freezing-point is lowered nearly twice as much as in the case of an equimolecular solution of a non-electrolyte. This can only be explained by assuming the presence of *twice as many particles* in a solution containing a molecular weight of salt as in the same volume of a solution containing a molecular weight of sugar. In other words, we have reason to think that all or nearly all of the salt molecules are separated, each into two particles, when they are dissolved in water. Other electrolytes behave as salt does, while non-electrolytes act like sugar.

A careful study of the boiling-point shows twice as great an elevation in the case of electrolytes as in non-electrolytes, in proportion to the number of dissolved molecules. Similar evidence is afforded by the phenomena of osmotic pressure. The differences in the freezing-point, boiling-point, and osmotic pressure produced by equal numbers of molecules of electrolytes and non-electrolytes may all be explained by assuming that the dissolved molecules in electrolytes are broken up or *dissociated* into parts. In non-electrolytes the molecules of the dissolved substance are not dissociated.

Dissocia-
tion of
electro-
lytes

98. Chemical Activity of Electrolytes.—We have already noted the fact that acids, bases, and salts are electrolytes; these are the substances that we have made use of in the greater part of our chemical actions so far. Nearly all chemical actions require the presence of water. When two solutions of electrolytes are mixed, action takes place at once if one of the products of the reaction is either insoluble or gaseous. So we may say that in general electrolytes are very active chemically. Non-electrolytes show very little activity.

99. Ions. — We find in the electrolysis of a dilute solution of hydrochloric acid that the hydrogen is liberated at the cathode and chlorine at the anode. To these moving particles in the electrolyte Faraday gave the name *ions*, meaning wanderers. We have just seen that the hydrochloric acid molecule is broken up, in the act of dissolving, into two particles, and since atoms are chemically indivisible, these must be the hydrogen and chlorine atoms. Why do they move in opposite directions? Bodies with electrical charges of opposite kind attract each other. Since the hydrogen particles in a water solution are attracted toward the cathode, or negative pole, when an electric current is passed, these hydrogen particles must be positively charged. Similarly the chlorine particles must have negative charges, since they are drawn toward the positive pole or anode.

When a solution of copper sulphate is electrolyzed, copper appears at the cathode and experimental evidence shows the presence of sulphur and oxygen at the anode. The copper sulphate must therefore dissociate into Cu, a positive (+) ion, and SO_4 , a negative (−) ion. *An ion, then, is either an atom or group of atoms carrying an electric charge.*

100. Explanation of Electrolysis. — Sodium chloride dissociates in water into sodium and chlorine ions. From the intensity with which sodium ordinarily reacts with water, we might expect the instant formation of sodium hydroxide. But this cannot be present, for the solution is perfectly neutral in reaction. The sodium *ion* does not react with water. But when a current is passed through a solution, the positive charges of the sodium ions are neutralized by the negative electrification of the cathode; the sodium

ions then become sodium *atoms* and react with the water surrounding the cathode, forming sodium hydroxide. It should be understood, however, that the electric current is not the cause of the dissociation into charged particles, but simply determines the direction in which they move. The dissociation took place while the substance was dissolving.

The chlorine ions give up their negative charges the instant they touch the anode, neutralizing in part the positive charge on that electrode. The particles of chlorine without their charges are ordinary atoms, which unite in pairs to form molecules of chlorine gas which bubbles off at the anode.

101. Differences between Ion and Atom. — The existence of an electric charge on an atom entirely changes its properties, as may be seen from the electrolysis of sodium chloride just described. Chlorine atoms decompose water by combining with the hydrogen and setting free the oxygen. Chlorine ions, however, move freely about in water without decomposing it. Atoms of chlorine tend to combine in pairs to form molecules of chlorine gas; ions of chlorine repel each other because they possess like charges.

The differences between ion and atom may now be stated: first, an ion has an electric charge, an atom has not; second, a single ion often includes several atoms of different elements. The electric charges on ions are very heavy, hence their energy supply is very different from that of atoms. The properties of bodies depend upon their energy supply, and this accounts for the difference in activity of the ion and the atom of the same element.

102. Ionization of Acids and Bases. — When an electrolyte is dissolved in water, some of its molecules enter the solution undissociated, while the other molecules separate into particles which become electrically charged in the process. On passing the current through a solution of hydrochloric acid, we find hydrogen collecting at the cathode and chlorine at the anode. In the solution there must be positively charged hydrogen ions and negatively charged chlorine ions. The electrolysis of nitric acid reveals the presence of hydrogen ions and NO_3 ions; that of sulphuric acid shows two hydrogen ions and one SO_4 ion for each molecule dissociated. The electrolysis of other acids gives, in every case, hydrogen at the cathode and so indicates the presence of hydrogen ions. To these are ascribed the characteristic properties of acids. This hydrogen ion, common to all acids, is responsible for the sour taste, and the red effect on litmus. The presence of hydrogen in a compound does not make it an acid; the compound must give hydrogen ions in water solution. Liquid hydrogen chloride, free from water, fails to act as an acid, because none of its molecules are separated into hydrogen ions. *An acid is a hydrogen compound whose water solution contains hydrogen ions.*

When bases are dissolved in water, the metallic atom in the molecule becomes the positive ion and the hydroxyl group the negative ion. The hydroxyl ions are the only ions common to all bases, and to them the characteristic properties of bases are attributed. Hence our definition: *A base is a hydroxide whose water solution contains hydroxyl ions.*

103. Effect of Dilution on Ionization. — It will be readily seen that the more ions there are present in a given solu-

tion, the better it will conduct the current, for the ions act as carriers. So we can measure the degree of ionization by the conducting power of the solution, provided there is the same weight of solute between the electrodes in every case. Conductivity under these conditions is called molecular conductivity. We find, as we continue to dilute an electrolyte, the molecular conductivity increases up to a certain point, beyond which it does not change. This might be expected, for at a certain dilution all the molecules are dissociated, and a further dilution causes no further dissociation. The effect of dilution on the ionization of chloracetic acid is shown in the following table:

DILUTION.	IONIZATION.
47.25 grams per liter	5.4 %
11.81 grams per liter	10.57 %
2.95 grams per liter	20.00 %

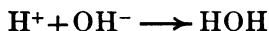
104. Activity of Acids and Bases. — The chemical activity of an acid depends upon the extent to which its dissolved molecules are dissociated into ions. Hydrochloric acid is almost wholly dissociated into its ions in dilute solution. This is why it acts vigorously on metals and neutralizes bases. Such an acid is spoken of as a *strong acid*. Nitric acid is another example of a strong acid. Sulphuric acid, which is dissociated but two-thirds as much as the acids just mentioned, is not so strong an acid. Acetic acid is the type of a weak acid, because it is so slightly dissociated (less than 2% in dilute solution) that it does not act vigorously on most metals, and its reactions with other substances are slow.

The term *strength of acid* must not be confused with

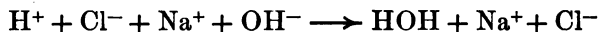
the term *concentrated acid*. Concentrated sulphuric acid usually contains about 98% H_2SO_4 , while concentrated hydrochloric contains but 37% HCl . Sulphuric acid, then, is usually the more concentrated, but it is the weaker acid of the two. Hydrochloric acid is the more reactive, since it is dissociated to a greater extent in water solution. The reason for the displacement of another acid by sulphuric acid is not that sulphuric acid is a stronger acid, but that it has a higher boiling-point.

As in the case of acids, the strength of a base depends upon the degree of ionization it undergoes in solution. Sodium hydroxide and potassium hydroxide are almost completely dissociated in dilute solutions. They are types of strong bases.

105. Explanation of Neutralization.— When we mix dilute solutions of hydrochloric acid and sodium hydroxide, we have present in the mixture the positive ions, hydrogen and sodium, and the negative ions, chlorine and hydroxyl. Any change that takes place while the acid and base are in solution must consist in the union of oppositely charged ions to form undissociated or electrically neutral molecules. We have already seen that water is a non-electrolyte and can only be ionized to a very small extent. Now we have present in our solution hydrogen ions, each with one positive charge, and hydroxyl ions, each with an equal charge of negative electricity. Each positive hydrogen ion will attract a negative hydroxyl ion, and *vice versa*. The two ions combine, the equal opposite charges neutralize each other, and a molecule of undissociated water results. Indicating the sign of the charge by a + or – above and to the right of the symbol, we may express this charge by the equation:

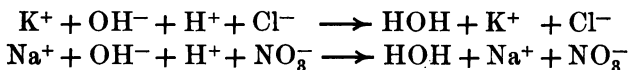


As the water formed is practically undissociated (only two molecules in a billion), we may consider it as completely removed from the action as if it had formed an insoluble compound or precipitate. In the neutralization, for each H^+ ion withdrawn in this way a Cl^- ion is left, and for each OH^- ion a Na^+ ion remains. These will not unite permanently so long as water is present, for the sodium chloride is dissociated as fast as it is formed. When the neutralization is complete, there are neither H^+ nor OH^- ions left to give an acid or a basic reaction, and the solution contains equal numbers of Na^+ and Cl^- ions. The equation showing these facts is:



If the solution is concentrated, the degree of dissociation is lessened, and Na^+ and Cl^- ions unite to form undissociated sodium chloride. When evaporation is complete, we find that they have completely united, forming crystals of salt.

106. Products of Neutralization.—We get similar results from the use of other acids and bases. Potassium hydroxide and hydrochloric acid give water, K^+ ions and Cl^- ions. Nitric acid and sodium hydroxide yield undissociated water, Na^+ ions and NO_3^- ions.



In every case of neutralization the products are:

- (1) undissociated water;
- (2) a solution containing positive ions from the base and negative ions from the acid;
- (3) energy in the form of heat.

During the evaporation of the solvent these ions unite to form a compound known as a *salt*.

107. Heat of Neutralization.—Neutralization, as a chemical process, is essentially the formation of undissociated water molecules. It is always accompanied by the liberation of heat. When dilute solutions, containing equal amounts of a strong acid, are neutralized by different strong bases, the same quantity of heat is produced in each case. This heat is known as the *heat of neutralization*.

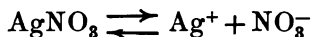
Table showing heat of neutralization expressed in calories:

	HCl	HNO ₃
NaOH	13,700 cal.	13,700 cal.
KOH	13,700 cal.	13,700 cal.

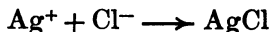
This uniformity in the heat of neutralization indicates an action that is common to all these cases. The only common product is water. *Therefore, the heat of neutralization is the heat of formation of water from hydrogen and hydroxyl ions.*

108. Other Actions between Ions.—Most chemical actions used in the laboratory take place in solution or in the presence of water. These are usually the reactions between the ions of acids, bases, and salts which are largely dissociated in solution. Such reactions are widely used to produce characteristic insoluble compounds in analytical chemistry.

The test for hydrochloric acid or a chloride is a search for the presence of chlorine ions. The solution of silver nitrate used in the test contains silver ions, viz.:

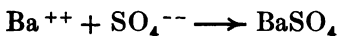


These positive silver ions will encounter negative chlorine ions if the solution tested contains a chloride. Silver chloride is formed. This compound, being practically insoluble and hence undissociated, separates as a precipitate. Therefore the equation is:



A solution of potassium chlorate also contains chlorine, not as a simple ion, but as part of the ion ClO_3^- . So when we mix this solution with the silver nitrate, we have the ions Ag^+ , NO_3^- , K^+ , ClO_3^- . Here no precipitation takes place, since the compounds, silver chlorate, AgClO_3 , and potassium nitrate, KNO_3 , that would be likely to form, are both soluble. Silver nitrate solution, then, is the test for the chlorine *ion*, and not for the chlorine *atom*.

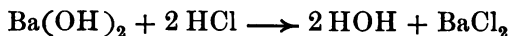
The test for a sulphate depends upon the combination of barium ions, Ba^{++} (from the barium chloride added), with the SO_4^{--} ion of the sulphate. The barium sulphate formed, is insoluble and separates as undissociated molecules. The equation is:



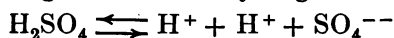
When the combination of ions in a chemical action produces an insoluble compound, the action tends to complete itself, or "run to an end." The precipitation of the undissociated molecules gradually removes the combining ions from solution and allows the further dissociation of the compounds producing them. The reaction is at an end when the supply of either of the combining ions is exhausted.

A reaction also completes itself when a combination of ions produces a substance, volatile under the existing conditions. The combining ions leave the solution in the undissociated molecules of the volatile substance.

109. Charges carried by Ions. — We have seen that one molecule of hydrochloric acid neutralizes one molecule of sodium hydroxide, producing one molecule of water. But we find that to neutralize one molecule of barium hydroxide, $\text{Ba}(\text{OH})_2$, two molecules of hydrochloric acid are required, according to the equation:



When neutralization is complete, the barium chloride is largely dissociated into barium and chlorine ions. In any solution the number of positive charges must equal the number of negative charges. Therefore, each barium ion must contain two positive charges to neutralize the negative charges on the two chlorine ions, with which it will unite when the solution is evaporated to get the salt. Sulphuric acid dissociates into H^+ , H^+ , and SO_4^{--} ions; the SO_4^{--} ion must carry two negative charges to balance the positive charges of the two hydrogen ions.

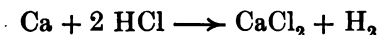


Some other ions carry three and even four charges.

NO. OF CHARGES.	POSITIVE IONS.	NEGATIVE IONS.
1	H, Na, K, Li, Ag, NH_4 , Cu (cuprous), Hg (mercurous)	OH, F, Cl, Br, I, NO_3 , ClO_3 , and other negative ions of monobasic acids
2	Ca, Sr, Ba, Mg, Zn, Hg, Co, Ni, Cu (cupric), Fe (ferrous), Sn (stannous)	S, SO_4 , CO_3 , and other negative ions of dibasic acids
3	Al, Bi, Sb, Fe (ferric)	PO_4 and other negative ions of tribasic acids
4	Sn (stannic)	SiO_4 and negative ions of tetrabasic acids

The preceding table shows the common ions with the number of charges carried by each and the signs of the charges.

110. Valence. — Atoms differ with respect to the number of atoms of other elements with which they combine. The difference in this combining power is indicated by the term *valence*. We have already seen that the hydrochloric acid molecule consists of one atom of hydrogen and one atom of chlorine. As this is the simplest combining relation possible, we take the valence of each of these elements as unity and call them *univalent* elements, since no other elements are found to have a less combining power. When one atom of any element combines with one atom of hydrogen or of chlorine, the valence of the element is one. The formulas NaCl, KCl, HBr, HI, show that sodium, potassium, bromine, and iodine are univalent elements. One atom of oxygen unites with two atoms of hydrogen, so the valence of oxygen is *two*. An atom of calcium replaces two atoms of hydrogen in hydrochloric acid and unites with two atoms of chlorine:



Hence the valence of calcium is *two*, or it is *bivalent*. We see in this case that the number of atoms of hydrogen *replaced* by one atom of an element measures the valence of that element. *The valence of an element is the number of hydrogen atoms which its atom will unite with or will replace.*

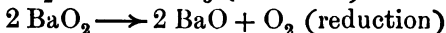
In ammonia, NH_3 , one atom of nitrogen is combined with three hydrogen atoms; in this compound, nitrogen has a valence of *three*, or it is *trivalent*. Marsh gas, CH_4 , contains four atoms of hydrogen combined with one atom

of carbon; therefore carbon has a valence of *four*; it is *quadrivalent*.

In electrolytes, the valence of each ion is numerically equal to the number of charges carried by it. This, of course, does not *explain* the valence of atoms in non-electrolytes, but does indicate a connection between the valence and the electrical capacity of an atom.

111. Variations in Valence.—An element may have more than one valence, according to the element with which it combines and the conditions under which combination takes place. The valence of hydrogen is always regarded as one, and that of oxygen generally as two. Sulphur has a valence of *two* in hydrogen sulphide, H_2S ; in sulphur dioxide, SO_2 , its valence is *four*, being twice that of oxygen; in sulphur trioxide, SO_3 , its valence is *six*.

The changes in valence, which take place during certain reactions, give an extended meaning to the terms *oxidation* and *reduction*, because such changes in valence are often brought about by the action of oxidizing and reducing agents:

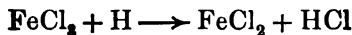


Hence the terms *oxidation* and *reduction* are often used to express increase or decrease in valence. In this

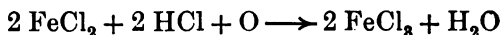
Oxidation and reduction. sense, *oxidation means an increase in the valence,*

and reduction a decrease in the valence, of an element. The terms, then, may be applied to reactions in

which oxygen takes no part. Thus if ferric chloride, FeCl_3 , is treated with nascent hydrogen, ferrous chloride, FeCl_2 , and hydrochloric acid are produced:



The iron atom is reduced from a valence of three in the ferric compound to a valence of two in the ferrous compound. By adding an oxidizing agent, such as nitric acid, to the mixture of ferrous chloride and hydrochloric acid, the ferrous chloride is *oxidized* to ferric chloride, by the addition of an atom of chlorine, thus increasing the valence of the iron:



112. Application of Valence.—Valence is useful in writing formulas and equations. Thus, knowing that both hydrogen and sodium are univalent, we know that it will take two sodium atoms to replace the two hydrogen atoms in sulphuric acid, H_2SO_4 , and that sodium sulphate will have the formula Na_2SO_4 . Similarly, as the valence of zinc is two, zinc sulphate is represented by the formula ZnSO_4 .

Summary.

Solutions are classified as *electrolytes* and *non-electrolytes*, according to their conducting power. The electrolytes include solutions of acids, bases, and salts.

The *effect of dissolved substances* on the boiling-point and freezing-point indicate that the molecules of the solute are dissociated in the case of electrolytes. Electrolytes are more active chemically than non-electrolytes.

The portions into which a molecule dissociates are *ions* and carry equal and opposite electric charges. When an electric current is passed through an electrolyte, each ion passes to the electrode of opposite sign and is there discharged and liberated. *Acids* furnish *hydrogen ions* in solution; *bases*, *hydroxyl ions*, and *salts* furnish *other ions*. The percentage of ionization increases with the dilution.

The *strong* or *active acids and bases* are those which are highly

dissociated. The essential action in *neutralization* is the union of the hydrogen and hydroxyl ions to form undissociated water ; during the evaporation, the union of the other ions to form a salt is completed. The strong acids and bases unite with the same heat of neutralization.

Chemical tests are often tests for ions. Hydrogen and metallic ions carry positive charges ; the non-metallic ions negative charges.

Elements differ in their *valence*. The hydrogen atom is the standard of valence. An element may have more than one valence under different conditions. The terms *oxidation* and *reduction* are sometimes applied to changes of valence.

Exercises.

1. How do you determine whether a given solution is an electrolyte?
2. When a beaker of acetic acid is put in circuit with an incandescent lamp, the lamp glows feebly, while the solution of sodium acetate allows it to glow brightly. What does this show?
3. Compare the freezing-point of sea-water with that of ordinary rain-water.
4. Why will substances often react with each other in solution while they will not in a dry state?
5. What ions are present in solutions of the following: KCl , ZnSO_4 , KClO_3 , NaOH .
6. Distinguish carefully between an ion of potassium and an atom of potassium.
7. Why is nitric acid a more active acid than sulphuric acid?
8. Give the changes that take place and the products formed in the following cases:
 - (a) when nitric acid is added to water;
 - (b) when a piece of caustic potash is dissolved in water;
 - (c) when the two solutions are mixed.

9. A piece of red litmus turns blue in a solution of sodium carbonate (Na_2CO_3). The presence of what ions is shown by this test?

10. Write equations, indicating ions, for the neutralization of potassium hydroxide with sulphuric acid; of nitric acid with ammonium hydroxide.

11. Will sodium chlorate (NaClO_3) give the test for chlorine ions with silver nitrate?

12. Give two conditions under which a reaction goes on to completion, and explain each.

CHAPTER XVI.

SODIUM AND POTASSIUM COMPOUNDS.

113. General Properties. — Just as sodium and potassium resemble each other very strongly, so the corresponding compounds which the two elements form have many points of similarity. For this reason these compounds can be advantageously studied together.

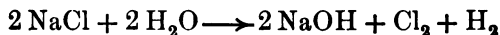
Most sodium and potassium compounds are white crystalline substances; practically all of them are soluble in water. With the exception of the hydroxides, all of those that we shall study are salts, possessing in a marked degree those properties which are characteristic of this class of bodies. As a rule they are very stable compounds. They are among our most common and useful substances.

Sodium compounds are generally less soluble in water than are the corresponding potassium compounds; they are, therefore, not so satisfactory for certain uses. On the other hand, sodium salts are usually cheaper than those of potassium. Moreover, since the atomic weight of sodium is 23, while that of potassium is 39, a gram of sodium salt contains a greater number of molecules than a gram of the corresponding potassium compound. Consequently a gram of sodium salt will "go farther" than a gram of the same potassium salt. For these reasons sodium compounds are generally used in manufacturing operations in preference to those of potassium.

114. Preparation of the Hydroxides (NaOH , KOH). — Two methods are in use for the manufacture of these

hydroxides. In describing the operations, the sodium compound will be taken as a type for both.

We saw (page 57) that a water solution of sodium chloride, on being decomposed by an electric current, gives chlorine, hydrogen, and sodium hydroxide as products :



The importance of sodium hydroxide is such that this operation is now carried out on a manufacturing scale. The apparatus shown in the diagram (Fig. 36) **Electrolysis of brine.** is used. The anodes are placed in solutions of salt in compartments *AA*, and the cathodes in

B. A layer of mercury (*MM*) permits the passage of a current between *A* and *B*, but prevents the mixing of the solutions.

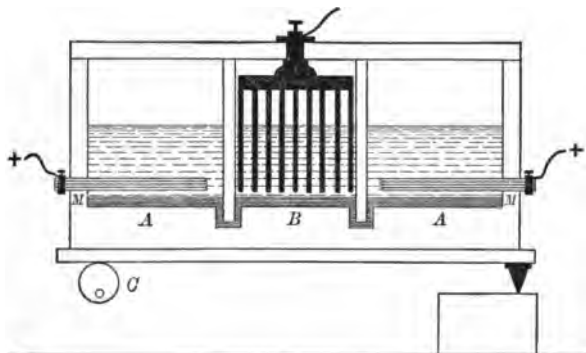


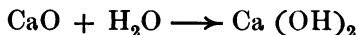
Fig. 36. Electrolytic preparation of sodium hydroxide.

On passing the current, chlorine is liberated at the anode, and passes off through a pipe, not shown in the figure. The positive sodium ions, moving toward the cathode, discharge against the mercury, and the metallic sodium, dissolving in the mercury, forms an amalgam which floats on the surface of the mercury.

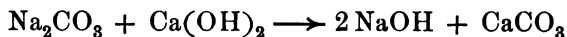
By rocking the tank by means of the cam *C*, the sodium amalgam is passed into the middle compartment *B*, where it reacts with the water, forming sodium hydroxide. The hydrogen which is set free is withdrawn by a pipe not shown in the figure.

In this way a strong solution of pure sodium hydroxide is obtained. The solution is drawn off, the water evaporated, and the sodium hydroxide obtained as a white solid. This is melted and cast into sticks or run into iron drums. The chlorine which is obtained as a *by-product* is used to make bleaching powder.

Calcium hydroxide, $\text{Ca}(\text{OH})_2$ (ordinary slaked lime), is
Lye made from calcium oxide, CaO (unslaked lime),
process. by adding water :



Calcium hydroxide is slightly soluble in water. If a solution of it is boiled with sodium carbonate, Na_2CO_3 , the following reaction occurs :



The calcium carbonate, CaCO_3 , formed is insoluble in water. It is this fact that makes the action possible. The solution of sodium hydroxide is separated from the precipitated calcium carbonate and evaporated to dryness.

115. Properties of the Hydroxides. — The hydroxides are very strong bases. As we have seen, they neutralize acids, forming salts and water. These bases have such a corrosive action on animal and vegetable matter that they are called *caustic* alkalis. Glass is attacked by them; and although the action is somewhat slow, a solu-

tion of either hydroxide on standing in a glass bottle becomes quite impure.

Sodium hydroxide, *caustic soda*, is manufactured in enormous quantities for use in soap-making. It is also used in making bleaching solutions and in numerous other operations. Potassium hydroxide, *caustic potash*, is not so extensively used in manufacturing operations. It is used to make other compounds of potassium, and in the preparation of some soaps.

Uses.

116. Sources of Sodium Chloride. — Sodium chloride, NaCl, *common salt*, is the most abundant sodium compound found in nature. Rock salt, or halite, is found in many countries, but the largest deposits are those in Louisiana, Austria, Germany, and Spain. Often in these beds the salt is of such purity that it has only to be mined and crushed to be ready for use.

Salt mines.

Much of the salt in this country is obtained from salt wells in New York, Michigan, Ohio, and several other states. A boring is made, and water sent down to the salt bed. There brine is formed and pumped to the surface. The earthy impurities in the brine settle, and then it is evaporated. A fairly pure salt is thus obtained.

Salt wells.

The total amount of salt found in deposits, however, is insignificant compared with the quantity contained in the seas and oceans. The percentage of salt in sea-water is small, yet it has been computed from the average per cent that the total quantity in the sea is 36,000,000,000,000,000 tons. The percentage of salt is not uniform for all seas and oceans. These variations depend upon the ratio existing between the amount of water delivered by rivers to a sea and the

Sea-water.

amount lost by evaporation. Thus, in the Baltic Sea, the inflow of river-water, which contains much less salt than sea-water, exceeds the loss by evaporation. Hence the water of the Baltic is relatively fresh. In the Dead Sea the reverse conditions prevail; evaporation exceeds the inflow, and a solution approaching saturation has resulted. The average amounts of salts contained in one hundred parts of sea-water are :

Dead Sea . .	22.0 parts	Atlantic Ocean .	3.6 parts
Mediterranean .	3.8 parts	Baltic	0.5 part

Extraction from Sea-Water. — The method employed for getting salt from sea-water depends upon the climate. In warm countries the sea-water is evaporated by the sun's heat in shallow basins. The salt crystallizing out is not very pure. In cold countries like Russia, sea-water is allowed to freeze in flat basins. The coating of ice, which contains very little salt, is removed, and the process repeated till a concentrated brine is obtained, which it will pay to evaporate by artificial heat.

117. Purification of Salt. — Common salt contains several impurities. The principal impurity is magnesium chloride, a deliquescent substance which causes ordinary salt to cake. To get the pure sodium chloride, hydrogen chloride is passed into a saturated brine, or concentrated hydrochloric acid is added. Pure salt separates, because it is less soluble in a solution of hydrochloric acid than in water.

118. Properties and Uses of Sodium Chloride. — Sodium chloride crystallizes in transparent cubes. Generally these cubes arrange themselves in four-sided, hollow pyramids known as *hopper crystals* (Fig. 37). Water is often

mechanically included in the crystals when salt separates from solution. When such crystals are heated, the enclosed water, being converted into steam, is violently expelled with a crackling noise and the flying about of small particles of salt. This action is known as *decrepitation*. Sodium chloride is but slightly more soluble in hot water than in cold. It vaporizes slowly at a red heat.

Sodium chloride is typical of one of the three great classes of chemical compounds. It was the first representative of its class to become familiar to man. Other compounds with properties similar to common salt became known as *salts*. For a long time the term *salt* meant a white substance soluble in water, with a taste resembling common salt. Many compounds now known as salts possess neither of these properties. A water solution of a salt, like sodium chloride, does not change the color of litmus. Like most salts, it is composed of a metallic element and a non-metallic constituent.

Salt is indispensable as a food for the higher animals. It furnishes the chlorine needed for the hydrochloric acid in the gastric juice. Tons of common salt are used every year in the preparation of sodium carbonate. This is its most important commercial use, but there are many minor uses.

119. Potassium Chloride.—The chloride of potassium, KCl, is also found in sea-water, but in smaller quantities

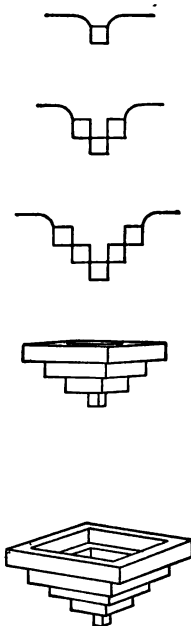


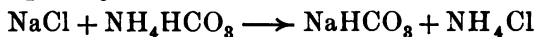
Fig. 37.

than sodium chloride. Plants also contain it in minute amounts. Its most important source is the mineral deposits at Stassfurt, Germany.

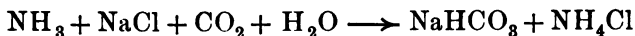
The properties of potassium chloride are similar to those of sodium chloride, but the potassium compound is more soluble in water. The chloride is used in the manufacture of other potassium compounds, particularly the nitrate and chlorate.

120. Occurrence and Preparation of the Carbonates (Na_2CO_3 , K_2CO_3).—These important compounds occur only to a very limited extent in nature. The ashes of land plants contain potassium carbonate, and the ashes of sea plants sodium carbonate.

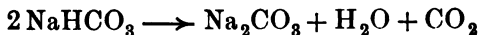
Sodium carbonate is manufactured from sodium chloride by the *Solvay process*. If a strong solution of sodium chloride is treated with ammonium bicarbonate, **Solvay process.** NH_4HCO_3 , a reaction occurs as follows :



The substance NaHCO_3 , sodium bicarbonate, is relatively insoluble in water. It will therefore be precipitated from the strong solutions used, and can be separated by filtration. In practice the operation is carried out by saturating a concentrated brine with ammonia and then passing carbon dioxide into this mixture under pressure:



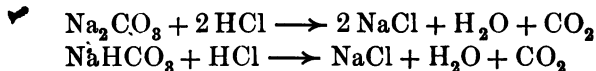
Sodium bicarbonate, NaHCO_3 , commonly known as *baking soda*, can be converted into sodium carbonate, Na_2CO_3 , *washing soda*, by heat:



It is a matter of great importance to produce sodium carbonate at low cost. For this reason the above reactions

are carried out so that the by-products are utilized. The ammonium chloride is used to furnish ammonia to saturate a fresh supply of brine. The carbon dioxide that is given off in decomposing sodium bicarbonate furnishes part of that needed in the first step of the operation.

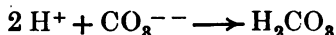
121. Uses of the Carbonates.—Two of the uses of the carbonates of sodium have been implied in the names washing soda and baking soda. The former has, in a modified way, the properties of sodium hydroxide. In the refining of petroleum, sodium carbonate is used to neutralize sulphuric acid. It dissolves many substances, especially oils or fats, and hence it is an excellent cleansing substance. It is usually an important constituent of cleaning powders. Both washing soda and baking soda liberate carbon dioxide when treated with acids:



We see from these equations that for equal weights of the carbonates, baking soda furnishes the greater amount of carbon dioxide. It is consequently preferred for those uses, as baking powder, where the liberation of carbon dioxide is required.

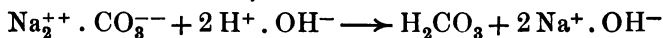
122. Hydrolysis.—A water solution of sodium carbonate is not neutral, but alkaline. This depends upon the slight dissociation of water, a condition which was not taken into account in the discussion of the dissociation of compounds. In most cases the few hydrogen and hydroxyl ions from the dissociation of the solvent have little effect, but their presence must be reckoned with when the solution contains a compound which is but slightly more dissociated.

than water itself, *e. g.* carbonic acid, H_2CO_3 . When sodium carbonate, one of its salts, dissolves, it largely dissociates into Na^+ ions and CO_3^{--} ions. All of the hydrogen ions from the water, however, cannot remain as such in the presence of CO_3^{--} ions, because undissociated carbonic acid will be formed:



The withdrawal of the hydrogen ions to form an undissociated compound disturbs the equilibrium of water with its ions, and a few molecules of water will have to dissociate to restore it. Most of the newly formed hydrogen ions likewise pass into the undissociated carbonic acid. This process of dissociation and combination is repeated till an equilibrium is established. It must be remembered, however, that the progressive dissociation of water gave OH^- ions as well as H^+ ions. These hydroxyl ions have little tendency to combine with the Na^+ ions to form undissociated sodium hydroxide, but simply remain in solution as ions of this strongly dissociated compound. There are enough of these hydroxyl ions to give the blue reaction with litmus.

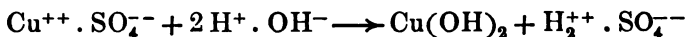
The total change which occurred may be expressed by the equation:



Such a change, involving water, is known as *hydrolysis*, and is the reverse of neutralization. Carbonic acid, being but slightly dissociated in water solution, is a weak acid, while sodium hydroxide is a strongly dissociated base. Hence sodium carbonate is a *salt formed by a weak acid with a strong base*. Such salts undergo hydrolysis when dissolved in water, and their solutions give alkaline reactions.

Sodium acetate, sodium cyanide, and sodium sulphide are salts of this character.

Some salts, as copper sulphate, give an *acid* reaction in water solution. This is also a case of hydrolysis:



A detailed explanation would show that nearly all the OH^{-} ions from the dissociation of the water combine with the Cu^{++} ions to form undissociated copper hydroxide, a very *weak* base. The hydrogen ions from the water are present at the end of the hydrolysis as ions of the strongly dissociated sulphuric acid. These hydrogen ions give the red effect with litmus, and the acid reaction of a solution of copper sulphate is accounted for.

The acid reaction of solutions of such salts, *formed by a weak base with a strong acid*, is due to hydrolysis. Zinc sulphate and ferric chloride are salts of this kind.

Salts formed by strong acids with strong bases are not subject to hydrolysis, since their ions have little tendency to combine with the H^{+} and OH^{-} ions of water to form undissociated compounds. The solutions of such salts are neutral. Sodium chloride and potassium nitrate belong to this class.

In general, hydrolysis is possible with a salt only when either the acid or base forming it, or both, are weak.

123. Occurrence of the Nitrates (NaNO_3 , KNO_3).— Both sodium and potassium nitrates occur in small quantities in the soil. They are formed by nitrogenous organic matter decaying in contact with soluble sodium or potassium compounds.

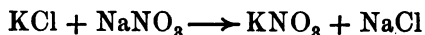
Deposits of sodium nitrate, covering an area of over four hundred square miles, are found in desert regions along the

western coast of South America. These beds lie near the boundary lines of Peru, Chile, and Bolivia and have

been the cause of many disputes between these **Nitre beds.**

The boundary lines have now been so adjusted that Chile owns the greater portion of these extremely valuable deposits. The crude nitrate is obtained by crushing the loose, rocky material of the beds and boiling it in hot water. The liquor containing the nitrate is run off and allowed to crystallize. The product, crude Chile saltpeter, contains 94 % to 98 % of sodium nitrate. A purer quality is obtained by recrystallization.

124. Manufacture of Potassium Nitrate.—Most of the potassium nitrate now used is prepared from sodium nitrate. The potassium compound is made by mixing hot, concentrated solutions of sodium nitrate and potassium chloride. The equation for the reaction is:



On evaporation the boiling mixture first deposits common salt, since this substance is less soluble in boiling water than is potassium nitrate. On cooling the solution, however, the potassium nitrate crystallizes out, because it is far less soluble in cold than in hot water. A purer quality of potassium nitrate can be obtained by recrystallization.

125. Properties and Uses of the Nitrates.—Sodium and potassium nitrates are white, soluble salts. Sodium nitrate differs from the potassium compound in crystalline form and in being hygroscopic. Both nitrates give off oxygen when heated, leaving compounds containing less oxygen, known as nitrites.

The principal use of potassium nitrate (ordinary saltpeter) is in the manufacture of black gunpowder. Sodium

nitrate is too hygroscopic for this purpose. Potassium nitrate is used to preserve meat, and corned beef owes its red color to this treatment. The cheaper sodium nitrate has replaced potassium nitrate in the manufacture of nitric acid and its derivatives. Chile saltpeter is also used as a fertilizer, and in the manufacture of sodium nitrite, a most important substance in the manufacture of aniline dyes.

Summary.

The *hydroxides* of sodium and potassium are prepared by the electrolysis of solutions of the chlorides, or by the reaction of the carbonate with slaked lime.

The *chlorides* of these two metals occur in nature.

They are typical salts. They have a saline taste, are neutral, and result from the action of the corresponding acid and base.

Their uses are dietary and preservative and for the preparation of other sodium and potassium compounds.

The *carbonates* occur in plant ashes: sodium carbonate in marine plants; potassium carbonate in land plants.

They are commercially prepared by the decomposition of the bicarbonates by heat.

The carbonates are used in the preparation of soaps, washing-powders, glass, and other compounds.

The *bicarbonates* are made commercially by the action of carbon dioxide with ammoniacal brines.

They are only slightly soluble and are less corrosive than the carbonates.

The bicarbonates are used in the preparation of the carbonates. Sodium bicarbonate is a constituent of all baking powders and is used in the preparation of some aerated liquors.

Sodium *nitrate* is obtained from Chile. Potassium nitrate is formed by the reaction of potassium chloride with sodium nitrate.

Sodium nitrate is used to prepare potassium nitrate, also as a

fertilizer and as a source of nitric acid. Potassium nitrate is used in gunpowder.

Exercises.

1. How could you tell potassium nitrate from sodium nitrate?
2. How are the nitrates produced in nature?
3. How could you show that there are potassium compounds in plants?
4. Why was sodium carbonate obtained from the ashes of sea plants and not from the water directly?
5. Write the equations for the preparation of sodium carbonate by the Solvay process.
6. In the Solvay process, why is not the normal carbonate produced directly, instead of forming the bicarbonate and then decomposing it?
7. What advantage has baking soda over potassium bicarbonate?
8. Equal weights being taken, which will neutralize the larger quantity of acid, sodium hydroxide or potassium hydroxide? sodium carbonate or bicarbonate?
9. Why is "soda" used in cleaning?

CHAPTER XVII.

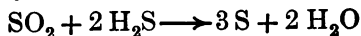
SULPHUR AND HYDROGEN SULPHIDE.

SULPHUR.

126. Occurrence. — Sulphur is found in nature both free and in combination with other elements. In the uncombined or *native* state it is found in volcanic regions. A specimen of native sulphur shows the element permeating a mass of calcium sulphate or calcium carbonate. Sulphur is also formed by chemical decomposition brought about by bacteria. Important deposits of this character occur in Louisiana.

Sulphur is found combined with many different metals, as sulphides; those of iron, copper, lead, and zinc are the most abundant. The sulphates of a few metals are found in considerable quantities.

127. Preparation. — The presence of uncombined sulphur in the neighborhood of volcanoes is probably accounted for by the interaction of two gases, hydrogen sulphide and sulphur dioxide, both of which are likely to be produced by volcanic action:



This reaction can easily be shown in the laboratory by bringing bottles of the two moist gases mouth to mouth. An action immediately occurs, and as a result sulphur is deposited on the sides of the bottles. The same thing can be shown in a more marked manner by using the apparatus represented in Figure 38.

Commercial Forms. — Sulphur is an important article of commerce. It can be bought in two different forms, *roll sulphur* and *flowers of sulphur*. The two forms are prepared in the same operation. This begins with the extraction of sulphur from the rocky material with which it is associated. The ore is heaped in piles and heated with-

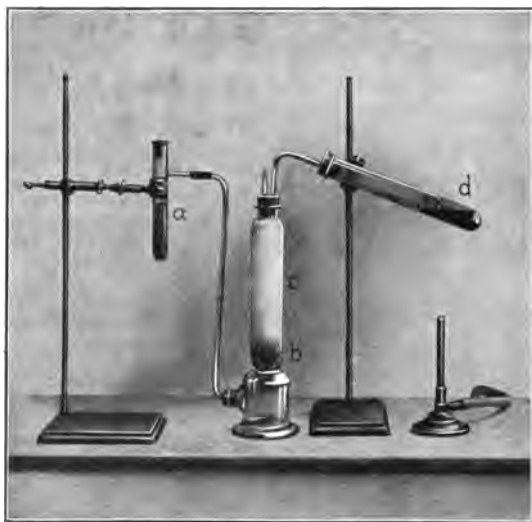


Fig. 38. Sulphur deposition.

a, hydrogen sulphide generator; b, moistened glass wool; c, jar with deposited sulphur; d, sulphur dioxide generator.

out access of air, until the sulphur melts and thus separates from the rock (Fig. 39). The sulphur is then further purified by heating it in iron vessels (retorts) without access of air, until it is vaporized (Fig. 40). The vapor is led into brick-lined rooms. A part of the gas is suddenly cooled and is deposited as a fine powder on the sides of the room. This form is known as flowers of sul-

phur. Most of the sulphur vapor condenses in the liquid form, and flows down to the outlet of the condensing chamber. It is then run into wooden moulds, where it solidifies into cylindrical-shaped rods about an inch and a half in diameter. This form is called roll sulphur or brimstone. Flowers of sulphur differ slightly in chemical properties from roll sulphur.



Fig. 39. Extraction of sulphur.

a, covering of spent ore; *b*, draught holes; *c*, slope down which sulphur runs; *d*, collecting pool.

128. Allotropic Forms.—No element displays a greater

variety of allotropic forms than sulphur. Three of these are well known and easily obtained by the following methods:

(1) Crystallization from carbon disulphide.

Carbon disulphide dissolves powdered roll sulphur very readily. The solvent evaporates quickly at ordinary temperatures; so that if such a solution stands, the sulphur soon begins to be deposited, just as salt is deposited when a solution of salt is evapo-

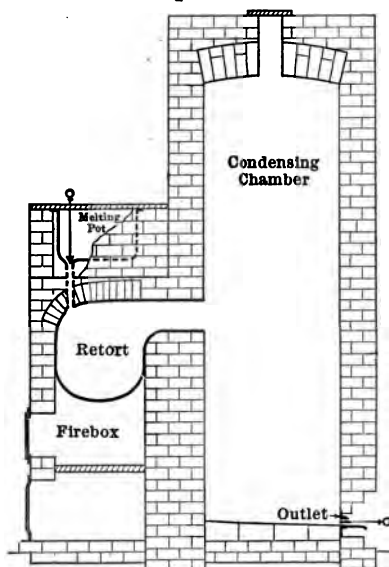


Fig. 40. Purification of sulphur.

rated. The sulphur is deposited in crystals of a beautifully regular octahedral shape. This form is *orthorhombic* sulphur (Fig. 41). It is soluble in carbon disulphide, and has a density of 2.01.

(2) Crystallization of melted sulphur.

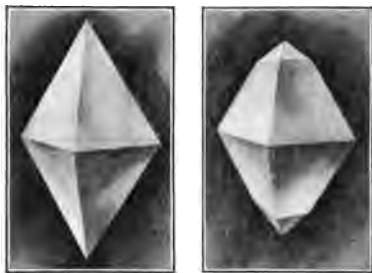


Fig. 41. Rhombic sulphur crystals.

Sulphur is melted and then allowed to cool until crystals appear at the surface; on pouring off the still liquid sulphur, the solid part is found in crystals shaped like long, narrow prisms with sharp ends (Fig. 42).

This kind of sulphur is known as *prismatic* sulphur. Its density is 1.96, and it differs in other properties from the rhombic variety. The prismatic form is unstable. On standing a few days, its crystals lose their transparency, become more brittle, and increase in density. Examination by polarized light shows that the long, narrow prisms have broken up into minute rhombic crystals.

(3) Sudden cooling of boiling sulphur.

By application of considerable heat sulphur can be made to boil. Before it reaches its boiling-point (450°) it goes through some interesting and unusual changes. When just above its melting-point, sulphur is a mobile liquid of a light amber color. As the temperature rises it darkens rapidly and thickens so that it can hardly be poured from the inverted test-tube; on further heating the sulphur again becomes less viscous, and finally boils, forming a pale yellowish-brown vapor.

When boiling sulphur is poured into cold water, the

cooled sulphur assumes a form (Fig. 43) altogether different in appearance from those already described. It is without crystalline form, of a rubber-like consistency, and light amber in color. Because of its lack of crystalline form it is called *amorphous* sulphur. This differs from the crystalline form in being insoluble in carbon disulphide. It is sometimes spoken of as plastic sulphur.

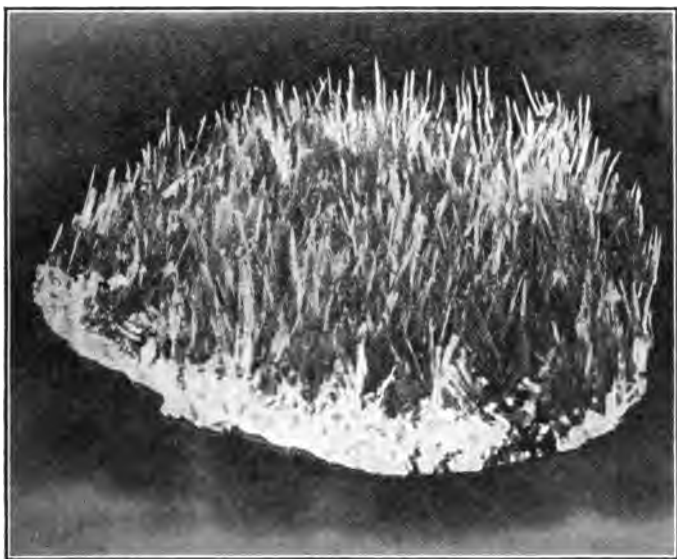


Fig. 42. Prismatic sulphur.

Like prismatic sulphur, it is unstable and is changed in the course of a few days into the stable rhombic form. In this change the amorphous sulphur loses its plastic character and becomes soluble in carbon disulphide.

If sulphur is dissolved in some alkali, as sodium hydroxide, and hydrochloric acid added to the solution, a white, finely divided precipitate is obtained. This precipi-

tate is a form of amorphous sulphur. When shaken with water it gives a fluid known as *milk of sulphur*.

129. Stability of the Allotropic Forms.—At temperatures up to 96° C. all forms of sulphur tend to assume the rhombic form. From 96° to 114°



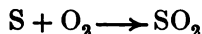
Fig. 43. Amorphous sulphur.

the stable form is the prismatic variety. If crystals of the rhombic variety are put into a test-tube and kept standing in boiling water for several days, the form will be changed to minute crystals of the prismatic variety. Thus it is seen that the form which the sulphur assumes depends on the temperature. It is generally true that each of

the allotropic forms of any element is stable under certain definite conditions.

Roll sulphur consists entirely of the rhombic variety. Flowers of sulphur are made up of the rhombic form together with a smaller proportion of the amorphous form, as is shown by the fact that flowers of sulphur are only partly soluble in carbon disulphide.

130. Chemical Properties.—All forms of sulphur burn readily when heated in the presence of oxygen; sulphur dioxide is formed as a product of the action. Sulphur is capable of taking oxygen away from compounds:



It does not, however, make a very satisfactory reducing

agent, because it is apt to combine with the products of the reduction.

Sulphur is a moderately active element. It combines readily with many metals, often with the evolution of light and heat. In a sense, then, it may be said to support combustion. This can be shown by heating sulphur in a test-tube until it boils and the sulphur vapor nearly fills the tube; on placing a strip of very thin copper in the tube, it takes fire and burns, copper sulphide being formed:



Powdered zinc and sulphur, if mixed in certain proportions, will unite almost explosively, with the formation of zinc sulphide (Fig. 44).



Sulphur does not unite very readily with non-metals. Such compounds are, in general, not very stable.

131. Sulphides.—The metallic sulphides form a very important class of compounds. Many metals are extracted from sulphide ores. Most of the sulphides, excepting those of the extremely metallic elements, are insoluble in water. They usually have characteristic colors. These facts are useful to the analytical chemist, for he can recognize the presence of certain metals by the color of their sulphides.



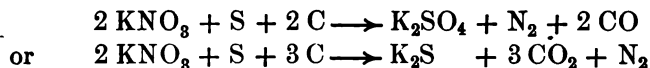
Fig. 44.

The blackening or tarnishing of metals is sometimes due to the action of sulphur. This is particularly true of silver. Sulphur or

sulphur compounds get into the air from illuminating gas or burning coal and, acting on silver, produces the black sulphide. Brass and copper are also readily tarnished by sulphur and some of its compounds.

132. Resemblances of Sulphur to Other Elements. — In the ease with which it combines with other elements, particularly metals, sulphur resembles both chlorine and oxygen. Generally it displays the closer resemblance to oxygen. This is shown in comparing the solubility in water of oxides and sulphides. Those metals which form insoluble oxides also, as a rule, form insoluble sulphides.

133. Uses. — Sulphur is used in making certain kinds of matches; to furnish sulphur dioxide for bleaching or disinfecting purposes; and in gunpowder. This explosive is composed of potassium nitrate, sulphur, and carbon. The chemical action that occurs in the act of explosion is, in the main, an oxidizing and reducing action. The number of products formed is very large. The reaction is partly represented by the equation:



Sulphur or a compound of sulphur, the monochloride, is used in the hardening or vulcanizing of india-rubber.

HYDROGEN SULPHIDE.

134. Formation. — Hydrogen sulphide, H_2S , is formed slowly and in small quantity when hydrogen is passed over heated sulphur (Fig. 45). The presence of the gas is shown by the blackening of a strip of paper (*aa*) moistened with lead acetate. The difficulty of forming hydrogen sulphide by the direct union of the elements is

in strong contrast to the great readiness with which the hydrogen compounds, so far studied, are formed. The lack of a strong tendency of hydrogen and sulphur to combine indicates the unstable character of their product.

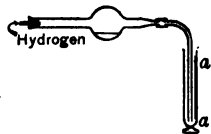


Fig. 45.

When albumen or other organic matter, containing sulphur, decays, hydrogen sulphide is one of the substances formed. If a little sulphur is added to fermenting sugar solution, hydrogen sulphide is produced.

135. Preparation.—Hydrogen sulphide is readily formed by the action of dilute hydrochloric acid on ferrous sulphide (Fig. 46):

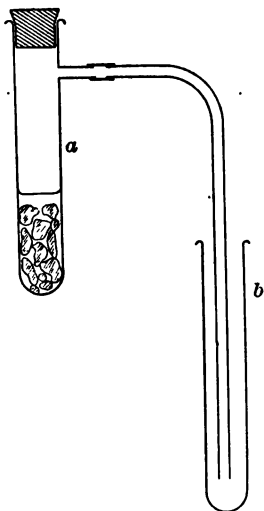
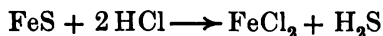


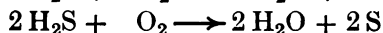
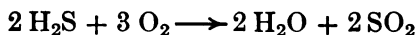
Fig. 46.

The hydrogen sulphide passes off readily as a gas; for this reason the double decomposition proceeds rapidly. The sulphides of some other metals could be used in place of the ferrous sulphide, and instead of hydrochloric acid dilute sulphuric acid might be used. In the figure, *a* is the test-tube generator containing iron sulphide and dilute hydrochloric acid, and *b* is the tube for collecting the gas by downward displacement.

136. Physical Properties.—Hydrogen sulphide is a colorless gas,

slightly heavier than air, having a characteristic odor resembling rotten eggs. It dissolves to some extent in water, and therefore is not usually collected over this liquid. It is generally collected by the displacement of air. A water solution of the gas is sometimes used in the laboratory, but in such a solution the gas is decomposed in a few days by action with the oxygen of the air. Besides being unpleasant, it is injurious to inhale the gas, as headache and sickness are apt to result.

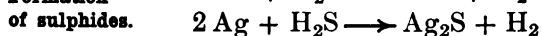
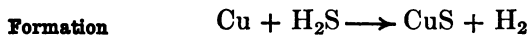
137. Chemical Properties. — The gas burns readily, if there is an ample supply of oxygen, forming water and sulphur dioxide; with a limited quantity of oxygen, sulphur is formed :



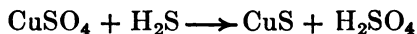
On being heated moderately, hydrogen sulphide breaks up into hydrogen and sulphur.

The fact that water solutions of hydrogen sulphide are poor conductors of electricity, shows it to be a weak acid. The solution reddens blue litmus very slowly, and the color is never as deep as that produced by solutions of strong acids.

Hydrogen sulphide acts on most metals, forming sulphides and liberating hydrogen :

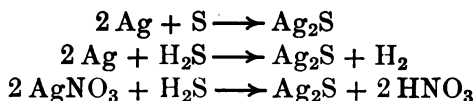


If hydrogen sulphide is passed into a solution of copper sulphate, copper sulphide is formed :



A similar reaction occurs with the dissolved salts of many metals, as lead, silver, and tin. In such cases the deter-

mining factor that makes the action possible is the insolubility of the metallic sulphide either in water or in the dilute acid that is formed as a result of the action. We have seen that metallic sulphides can generally be formed in three different ways, for example :

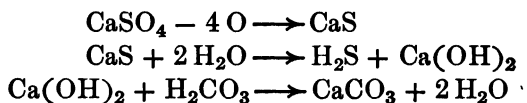


The possibility of precipitating metallic sulphides by this third method is of great value to the analytical chemist in determining the composition of unknown substances. The identification of the metal in a particular case is made by means of the color of the sulphide, its solubility in various reagents, or other characteristic reactions.

TABLE OF SULPHIDES.

NAME.	FORMULA.	COLOR.	DISSOLVES IN
Mercuric sulphide	HgS	Black	Aqua regia
Copper sulphide	CuS	Black	Concentrated nitric acid
Cadmium sulphide	CdS	Yellow	Concentrated nitric acid
Arsenic sulphide	As ₂ S ₃	Yellow	Yellow ammonium sulphide
Antimony sulphide	Sb ₂ S ₃	Orange	Yellow ammonium sulphide
Zinc sulphide	ZnS	White	Dilute acids

138. Sulphur Springs. — Hydrogen sulphide is produced in nature in several ways. We have mentioned its production during the decay of certain organic matter. Calcium sulphide is formed when decaying matter reduces calcium sulphate. Water reacts with calcium sulphide, forming calcium hydroxide and hydrogen sulphide; the calcium hydroxide is converted into the carbonate by the action of water containing carbon dioxide.



The presence of hydrogen sulphide in the waters of some sulphur springs is accounted for by these reactions.

Summary.

Sulphur is found native.

Commercial forms are roll sulphur and flowers of sulphur.

Rhombic sulphur, prismatic sulphur, and plastic or amorphous sulphur are allotropic forms.

	RHOMBIC SULPHUR.	PRISMATIC SULPHUR.
Specific gravity	2.07	1.96
Solubility	Soluble in carbon disulphide	Insoluble in carbon disulphide
Stability	Stable below 96°	Stable between 96° and 114°

Sulphur melts at 114° and boils at 450°; it is a non-conductor of electricity.

Sulphur is a moderately active element, burns in air, and unites directly with many elements.

Sulphur is used in the vulcanizing of rubber, in the manufacture of matches, and in the preparation of sulphur dioxide, sulphites, and carbon disulphide.

Hydrogen sulphide is prepared by the action of hydrochloric acid or of sulphuric acid with ferrous sulphide.

It occurs in volcanic gases and in water of sulphur springs, and is formed in nature by decay of organic matter containing sulphur.

Hydrogen sulphide is a colorless gas, poisonous, and possessing a characteristic disgusting odor.

One volume of water at 20° dissolves 3.1 volumes of hydrogen sulphide.

Its water solution is a weak acid which forms sulphides with most metallic ions.

It burns in a limited supply of air to form water and sulphur, and in an excess of air forms water and sulphur dioxide.

Hydrogen sulphide is used by chemists to precipitate certain metals, as sulphides, from solutions.

Exercises.

1. What conditions determine whether sulphur is to assume the prismatic or rhombic form?

2. Why is sulphur used in the manufacture of matches?

3. Write the formulas of five sulphides and the formulas of the corresponding oxides.

4. Starting with iron, sulphur, and hydrochloric acid, give directions for the preparation of hydrogen sulphide.

5. Calculate the weight of a liter of hydrogen sulphide measured under standard conditions.

6. How many grams of ferrous sulphide would be required for the preparation of five liters of hydrogen sulphide?

7. Under what conditions is sulphur deposited when hydrogen sulphide burns?

8. How many liters of oxygen would be required for the complete combustion of four liters of hydrogen sulphide?

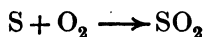
9. How many grams of hydrogen sulphide would be required to combine with the copper in 0.1 gram of copper sulphate?

CHAPTER XVIII.

OXIDES AND ACIDS OF SULPHUR.

SULPHUR DIOXIDE.

139. Preparation.— When sulphur burns in oxygen or in air, sulphur dioxide is formed:



The odor of burning sulphur is due to the dioxide formed.

Direct combination. Many ores are sulphides of metals, and large quantities of sulphur dioxide are prepared by roasting such ores in air.

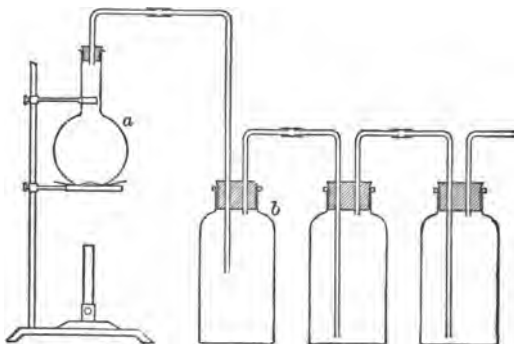
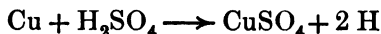


Fig. 47. Preparation of sulphur dioxide.

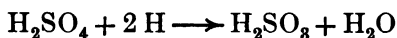
a, generator; *b*, safety bottle.

When copper, silver, or mercury is treated with hot, concentrated sulphuric acid, sulphur dioxide is formed (Fig. 47). The chemical action is complicated, but it is

probable that the acid first acts with the metal, and hydrogen is displaced, according to the equation:



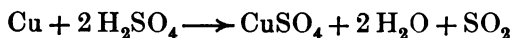
The hydrogen is then oxidized to water by the excess of hot, concentrated sulphuric acid. This reduction of the sulphuric acid to sulphurous acid, according to the equation: Reduction of sulphuric acid.



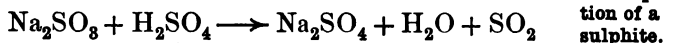
The sulphurous acid decomposes, as soon as it is formed, into water and sulphur dioxide, according to the equation:



The changes indicated in the three equations given above go on together. The total change may be represented by the one equation:

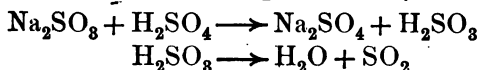


When a mixture of sodium sulphite and dilute sulphuric acid is gently heated in a flask, sulphur dioxide is evolved, according to the equation:



Decomposition of a sulphite.

Possibly sulphurous acid is first formed, but if so, this unstable compound immediately decomposes into water and sulphur dioxide. The equations are:



The evolution of the gas may be made very regular by using sodium acid sulphite and allowing sulphuric acid (1 to 1) to fall on it, drop by drop (Fig. 48).

140. Physical Properties.—Pure sulphur dioxide is a colorless gas, with a suffocating odor, and is more than

twice as heavy as air. It is very soluble in water; one volume of water dissolves many times its own volume of the gas at ordinary temperatures. The gas may be completely expelled from the solution by boiling.

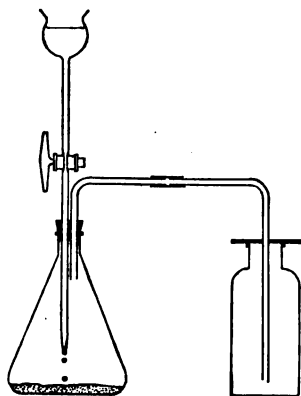
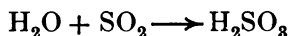


Fig. 48.

Sulphur dioxide is one of the easiest gases to liquefy. At ordinary temperatures a pressure of but two atmospheres is required; at the temperature of a freezing mixture of ice and salt, the ordinary atmospheric pressure is sufficient to change the gas to a liquid. Liquid sulphur dioxide is sold in glass or metal siphons (Fig. 49).

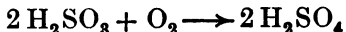
141. Chemical Properties.—The solution of sulphur dioxide has an acid reaction and neutralizes bases, forming sulphites. Thus with sodium hydroxide the reaction results in the formation of sodium sulphite and water. This indicates the presence in the solution of hydrogen and sulphite ions, or, in other words, the solution contains sulphurous acid. This acid, however, has never been separated from the solution. The acid is formed according to the equation:



Since sulphur dioxide unites with water to form an acid, **acid** it is called an *acid anhydride*. An anhydride is **anhydride**. named from the acid it forms with water. Hence sulphur dioxide is called sulphurous anhydride.

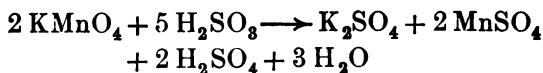
If a solution of sulphurous acid is allowed to stand

in contact with air, it gradually takes up oxygen, forming sulphuric acid, according to the equation:



Sulphites are likewise changed to sulphates.

Since sulphurous acid is so readily oxidized, it acts as a reducing agent in many cases. Potassium permanganate is reduced to potassium sulphate and manganese sulphate: Reducing action.



Chromic acid is reduced to chromium sulphate. This reducing action, in the presence of water, probably explains the bleaching action of sulphur dioxide in some cases. The coloring matter is reduced, thus decolorizing the substance. In other cases the sulphur dioxide unites directly with the coloring matter, producing a colorless compound. The color of materials bleached by sulphur dioxide will often return on exposure to the air. Bleaching by chlorine is more permanent.



Fig. 49.

142. Uses. — Great quantities of sulphur dioxide or of sulphites are used in the *bleaching* of many organic coloring matters. Straw, silk, wool, and other materials, which chlorine bleaching makes hard and brittle, are decolorized by sulphur dioxide (Fig. 50). Cherries are sometimes bleached with sulphurous acid and then colored with the

bright shades that are seen in the canned goods of commerce.

Sulphur dioxide is also used as a *disinfectant*. For this purpose sulphur is burned, or liquid sulphur dioxide is

allowed to evaporate in the room to be disinfected. In either case the room should be tightly closed and the air in the room be kept moist, so that the disease germs may be killed by the sulphurous acid formed. This power of sulphurous acid to kill lower organisms is the reason for its use in the *curing* of wine and beer. The growth of mould is thus prevented. An increasing



Fig. 50.

A carnation in air (a) and in sulphur dioxide (b).

but questionable use of the acid is its employment as a food preservative. Sulphur dioxide not only attacks lower organisms, but is decidedly injurious to higher forms of life. Vegetable growth is blighted in the neighborhood of smelters and chemical works where the gas is generated. In cities the gases from the burning of coal containing sulphur have a like effect.

The most important use of sulphur dioxide, however, is in the *manufacture of sulphuric acid*. Immense quantities are used for this purpose.

143. Sulphur Trioxide.—Sulphur trioxide is prepared by the oxidation of sulphur dioxide. It is formed in small quantities when sulphur burns, and its presence causes the cloudiness often observed in sulphur dioxide. This oxida-

tion may be made more rapid by the presence of catalytic agents. Finely divided platinum and ferric oxide are the most important ones. Platinized asbestos is prepared by soaking asbestos in platinum chloride and heating until finely divided platinum is left in the asbestos. A mixture of sulphur dioxide and air is passed over platinized asbestos (Fig. 51). The temperature must be carefully regulated, as the trioxide decomposes at a temperature only a little higher than that necessary for its formation. The reaction is then reversible and may be represented :

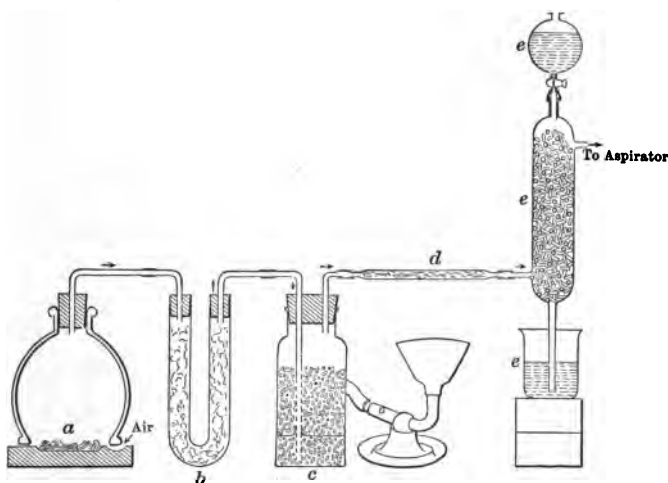
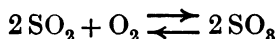
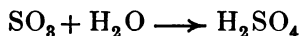


Fig. 51. Laboratory preparation of sulphur trioxide.

Sulphur trioxide (sulphuric anhydride) dissolves in water, forming sulphuric acid :

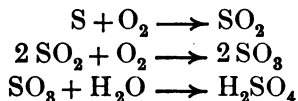


The laboratory preparation of sulphur trioxide and sul-

phuric acid by the contact method is represented in Fig 51. Sulphur (*a*) burns in the air drawn into the apparatus by an aspirator, and the sulphur dioxide formed passes with the excess of air into the U-tube (*b*) which is filled with some loose material to rid the gases of sulphur dust. In the bottle (*c*) the gases lose their moisture as they make their way through the glass beads drenched with concentrated sulphuric acid. The platinized asbestos in the tube (*d*) is gently heated, and brings about the union of the sulphur dioxide with the oxygen of the air. The sulphur trioxide resulting from the action is absorbed by concentrated sulphuric acid trickling down through the apparatus (*e*). Water may be used for this last absorption, but this makes the process longer.

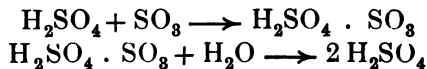
SULPHURIC ACID.

144. Preparation. — Commercially sulphuric acid is prepared by the method just stated (cf. 143). Sulphur, or ores containing sulphur, are burned in air. The sulphur dioxide and the other gaseous products of the combustion are cooled, freed from dust, arsenic, and most of the moisture, then mixed with air and passed through a tube containing a catalytic agent, usually finely divided platinum (Fig. 52). The oxygen of the air combines with the sulphur dioxide and forms the trioxide, which is then combined with water to form sulphuric acid :



In practice sulphur trioxide is passed into concentrated sulphuric acid, as it does not dissolve readily in water.

The solution is then diluted :



145. Physical Properties.—Sulphuric acid is a heavy, oily liquid. Ordinary commercial sulphuric acid, called oil of vitriol, is nearly twice as heavy as water. It boils at a higher temperature (338°) than most of the common acids, and many of its uses depend on this fact.

146. Chemical Properties.—Sulphuric acid mixes with water in all proportions; during the mixing considerable heat is evolved. If such a mixture is made, *the acid should be slowly poured and stirred into the water*. If the water is poured into the heavier acid, they cannot mix so readily, and a sudden generation of steam may cause spattering or break the vessel.

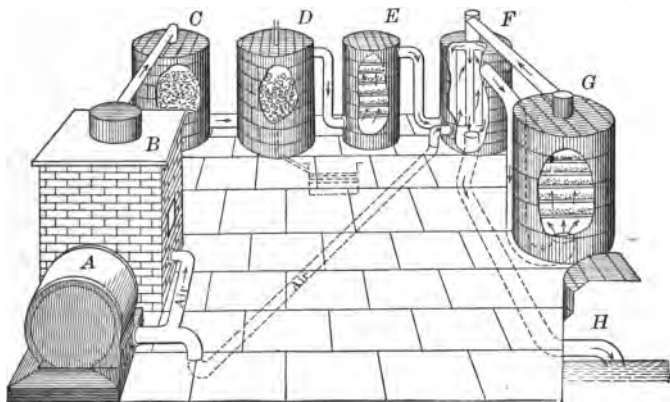
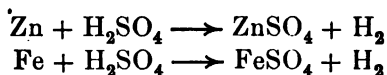


Fig. 52. Contact process (diagrammatic).

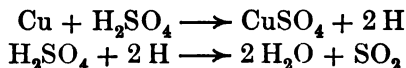
A, blower; B, pyrites burner; C, dry scrubber filled with coke; D, wet scrubber filled with coke wet with sulphuric acid; E, arsenic purifier; F, heater; G, contact chamber; H, absorber (concentrated sulphuric acid).

Concentrated sulphuric acid absorbs moisture from the air, and this tendency of the acid to take up water explains **Dehydrating** many of its actions. Wood, paper, sugar, and **action.** similar substances, containing hydrogen and oxygen, are charred by sulphuric acid. The acid removes the hydrogen and oxygen to form water, leaving a residue consisting largely of carbon. On the flesh it acts similarly, and a painful wound results.

With metals the acid acts in two ways. If the action takes place at a low temperature, hydrogen is evolved, **Action with** provided sufficient water is present to dissolve **metals.** the metallic sulphate formed:

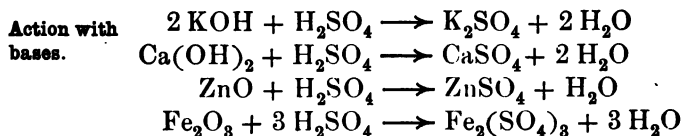


Mercury, silver, and copper are not acted on by the cold acid, but if concentrated acid is used and the temperature raised sufficiently, they react, reducing part of the sulphuric acid, forming sulphur dioxide, water, and metallic sulphates:

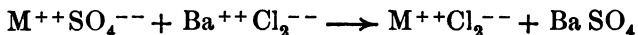


Thus at ordinary temperatures sulphuric acid acts like hydrochloric acid, exchanging its hydrogen for metals, but when hot and concentrated, it acts also as an oxidizing agent.

With bases and metallic oxides it reacts, forming water and sulphates:



147. Test for a Sulphate. — The sulphates are all soluble except four, the sulphates of barium, strontium, calcium, and lead. In detecting the SO_4 ion, a solution of barium chloride is usually employed. Representing by M^{++} any ion carrying two positive charges:



The barium sulphate is easily identified, because it is white and insoluble in water, dilute acids, and alkalis. The method is to test, with dilute hydrochloric acid, the solubility of the precipitate formed with the barium chloride.

148. Uses. — The absorption of water by sulphuric acid renders it a good dehydrating agent, and in the laboratory gases are dried by being made to bubble through it (Fig. 19, *b*). In the manufacture of sulphuric acid the air and sulphur dioxide employed are dried by contact with sulphuric acid. In the purification of petroleum products, kerosene, etc., it is used to remove, by charring, materials which would give offensive odors in burning. In the preparation of nitroglycerine it removes water from the nitric acid and glycerine.

As sulphuric acid has a higher boiling-point than most acids, it is used in their preparation. Examples of this action have already been studied (§§ 58, 135).

On account of the conductivity of its solutions, sulphuric acid is used in storage batteries and in plating. It is used also as a catalytic agent in the production of glucose from starch and water.

As a solvent it is used in cleaning metals, previous to tinning or galvanizing, and certain phosphate rocks are decomposed and made soluble and suitable for fertilizers by it. Enormous quantities of it are used in these opera-

tions, and in hundreds of others. *There are few materials in common use by civilized man with which sulphuric acid has not been directly or indirectly connected.*

Summary.

Sulphur dioxide can be prepared in several ways:

Direct combination of oxygen with free sulphur or with sulphur in sulphides; reduction of sulphuric acid; decomposition of sulphites with acids.

The characteristic odor, the weight, and the solubility in water are three striking physical properties of sulphur dioxide. Chemically it is an acid anhydride, forming sulphurous acid, which is a powerful reducing agent.

Sulphur dioxide is used in bleaching, as a disinfectant, as a food preservative, and, most important of all, in the manufacture of sulphuric acid.

Sulphur trioxide is prepared by the oxidation of sulphur dioxide by means of a catalytic agent.

Sulphur trioxide is the anhydride of sulphuric acid. It combines energetically with water.

Sulphuric acid is now manufactured by the "contact process," consisting of the following steps:

- (1) oxidation of sulphur to the dioxide;
- (2) catalytic oxidation of the sulphur dioxide to the trioxide;
- (3) dissolving the trioxide in concentrated sulphuric acid;
- (4) dilution of the last solution.

Sulphuric acid is a heavy, oily liquid of high boiling-point.

With metals sulphuric acid acts in two ways. At low temperatures and when dilute, hydrogen is evolved and the sulphate of the metal formed. When hot and concentrated, it acts on certain metals as an oxidizing agent, forming sulphur dioxide, water, and metallic sulphates. Sulphuric acid acts on bases and metallic oxides as a typical acid, forming water and a sulphate.

All *sulphates* are soluble in water, except those of lead, barium,

strontium, and calcium. To test for a sulphate, add a solution of barium chloride; a white, granular precipitate, insoluble in dilute hydrochloric acid, indicates the presence of sulphate ions.

Sulphuric acid is used as a dehydrating agent, in the preparation of other acids, and in a wide range of industrial applications.

Exercises.

1. Which of the laboratory methods would you use for preparing *pure* sulphur dioxide? Why?
2. If a bottle partly filled with concentrated sulphuric acid is left open to the air, the liquid contents increase. Explain.
3. What advantages has sulphur dioxide over chlorine as a bleaching agent? What disadvantage?
4. Explain why concentrated sulphuric acid must be poured slowly *into water* when the two liquids are mixed.
5. Account for the darkened rings formed on wood where bottles of concentrated sulphuric acid have been standing.
6. Why can either hydrochloric or sulphuric acid be used in the preparation of hydrosulphuric acid? Explain which of these two acids must be taken for the preparation of nitric acid.
7. Explain why boiling concentrated sulphuric acid produces such frightful burns.
8. Show how concentrated sulphuric acid acts as an oxidizing agent on metallic silver.
9. What effect would you expect if a strip of lead were placed in dilute sulphuric acid? Explain.
10. Why is a dish containing sulphuric acid put inside the case of a delicate balance? Why are clocks for keeping exact time similarly treated?
11. Why is the civilization of a country said to be indicated by the amount of sulphuric acid it uses?

12. Compare the chemical actions in chlorine and sulphur dioxide bleaching.

13. What is an acid anhydride? Name two anhydrides containing sulphur, and give their formulas.

14. How many pounds of sulphuric acid could be manufactured from 120 pounds of pure sulphur?

15. How many liters (standard conditions) of sulphur dioxide would result from the reaction of 12 grams of copper with concentrated sulphuric acid?

16. What weight of sodium sulphite must be decomposed to furnish 3.5 liters sulphur dioxide (standard conditions)?

17. Calculate how many grams (a) of silver sulphate and (b) of copper sulphate you could make from a dime which is 10 % copper. A dime weighs 2.48 grams.

CHAPTER XIX.

NITROGEN AND THE ATMOSPHERE.

149. Occurrence.—Nitrogen has already been mentioned as constituting a large portion of the atmosphere. It is also found in a few mineral compounds, many of which, however, are the result of the activity of animal and vegetable organisms. Nitrogenous organic compounds exist in great variety; and one class, the proteids, of which the white of egg is an example, are directly concerned with the life processes. In fact, nitrogen is perhaps the most characteristic element in living organisms, since the proteids make up the living matter of the muscles and the protoplasm of the cells. Life without nitrogen would be impossible. In the decay of organic matter much of its nitrogen is returned to the atmosphere in the form of the familiar gas ammonia.

150. Preparation. — Nitrogen may be prepared from air by causing oxygen to combine with phosphorus in the presence of water. Phosphorus is employed because its great tendency to combine with oxygen insures the completeness of the reaction, even at ordinary temperatures, and because its oxides have a great tendency to combine with water and so are rapidly removed from the vessel. In Fig. 53, *a* is a small crucible, floating on water, and containing phosphorus.

Other reducing agents may be used, provided the oxide formed is easily separated from the nitrogen. If air is

passed through a strongly heated tube containing reduced copper or fine-meshed copper gauze, nearly pure nitrogen results (Figs. 54 and 55). The reason for the use of copper is that its oxide is a non-volatile solid. Nitrogen prepared from air always contains argon and other impurities.

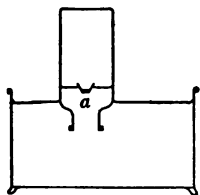
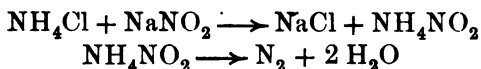


Fig. 53.

The oxidation of ammonia is a convenient method for preparing pure nitrogen. Ammonia gas is passed over strongly heated copper oxide. The hydrogen is oxidized to water, and the nitrogen remains. Heat alone will liberate nitrogen from its compounds. Ammonium nitrite, gently heated, decomposes into water and nitrogen. Owing to the unstable nature of ammonium nitrite, a mixture of ammonium chloride and sodium nitrite is used. Ammonium nitrite is probably formed and then decomposes, as just stated.



151. Physical Properties. — Nitrogen is slightly lighter than air, as we should expect from the fact that oxygen, the other chief constituent, is heavier. It is without color, odor, or taste. Nitrogen is less soluble in water than oxygen, so that the bubbles of gas given off, when ordinary water is warmed, contain a smaller proportion of nitrogen than air. Cooled to a very low temperature under atmospheric pressure, nitrogen becomes a colorless liquid; on further cooling the liquid freezes to a white solid.

152. Chemical Properties. — The large amount of nitrogen in the air is due to its inertness; it does not combine

readily with many substances, and its compounds are easily decomposed. It unites directly with few elements and with these only at high temperatures; sometimes the electric spark is necessary to cause combination. The ease and violence with which its compounds decompose is well illustrated by nitroglycerine and guncotton.

Nitrogen may be caused to combine slowly with oxygen by passing electric sparks through the mixture and removing the oxides by dissolving them in water as fast as they are formed. If they were not so **oxygen** removed, they would be decomposed by the heat of the

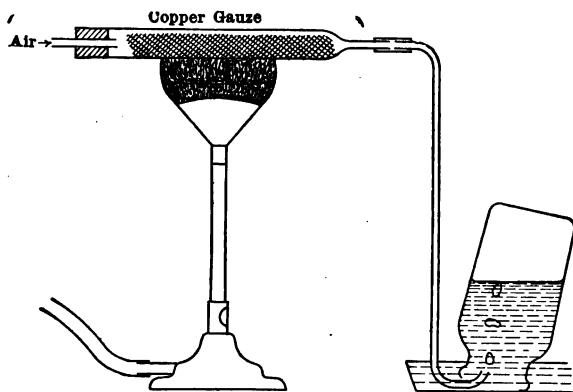
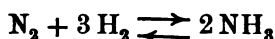


Fig. 54. Preparation of nitrogen.

succeeding sparks. Nitrogen will not burn in oxygen without a continual supply of external energy, as the temperature of the combustion is lower than the kindling-point of nitrogen. Such a combination of the oxygen and nitrogen of the air takes place in a flaming electric arc between metal poles.

Ammonia, (NH_3), can be formed by the passage of sparks through a mixture of hydrogen and nitrogen. In

this case, as in the similar production of the oxide, the ammonia must be removed as formed, since the reaction is reversible and a point of equilibrium is reached, at which it proceeds as rapidly in one direction as in the other:



A few *nitrides* are known, of which the principal ones are those of lithium, calcium, magnesium, and boron. These require a red heat for their formation. Magnesium nitride, the most common one, is a yellow powder formed by igniting magnesium and nitrogen.

While nitrogen does not react readily, many reactions are affected by its presence. Thus burning cannot be so vigorous in the air as in oxygen, since the large proportion of nitrogen dilutes the oxygen, preventing a rapid contact with the combustible material. Some heat is also employed in raising the temperature of the nitrogen; the temperature of combustion is lower than would be the case were nitrogen absent.

153. Composition of the Air. — The average proportions of the chief constituents of the air are as follows :

		COMPOSITION.	
		By volume.	By weight.
Nitrogen	. .	78.06	75.5
Oxygen	. .	21.00	23.2
Argon	. .	0.94	1.3
Carbon dioxide	. .	0.04	0.05

Traces of other substances are often present, but under the term *air* we usually include only the nitrogen, oxygen, and argon. The relative amounts of these are practically constant, except in certain localities, as in cities, and in poorly ventilated places.

154. Proofs that Air is a Mixture.— Air must be regarded as a mixture rather than a compound for several reasons:

(1) The composition is not absolutely uniform. This is not in agreement with the law of definite proportions. While the differences in composition are slight, they are greater than those found in different samples of a pure chemical compound.

(2) If the various components of the air are mixed in the proportions in which they are found in the atmosphere, there is no evidence of reaction. We have found that when a chemical change takes place, there is usually a change in the temperature caused by the absorption or liberation of heat. Other energy changes, such as the production of light and sound (explosions), often accompany reactions. None of these energy changes occur in this case, hence there is no probability of a reaction.

(3) If air is allowed to pass through an unglazed porcelain tube, it is found that the lighter nitrogen diffuses through the porcelain walls more rapidly than the oxygen; were they combined in molecules of a compound, they would go through with equal velocity.

(4) If air is cooled under pressure, it is found that the argon and oxygen liquefy before the nitrogen, and if the liquid air is allowed to evaporate, the nitrogen vaporizes more rapidly than the oxygen. If air were a compound, it would have a definite boiling-point, at which it would vaporize unchanged.

(5) When air is brought in contact with water, nitrogen and oxygen dissolve in the proportion of 63:34; while in atmospheric air the proportion is about 4:1 by volume.

The molecular motion of the gases and the winds suffice to keep the composition of the atmosphere practically constant. Local conditions may slightly affect the com-

position, especially in ill-ventilated places, but the total quantity of the air is so great — 15 pounds resting on each square inch of the earth — that even a large city produces scarcely any noticeable effect on the composition.

The constituents of air may be successively removed, so as to leave the nitrogen, by the apparatus represented in Fig. 55. The bottle (*a*) serves as an aspirator to draw air through the apparatus and also to collect the residual

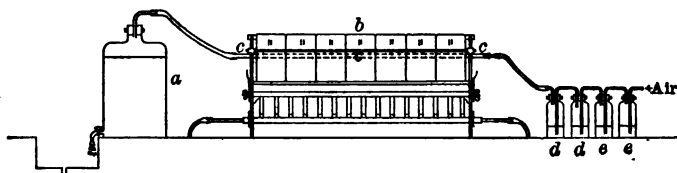


Fig. 55. Separation of the components of air.

nitrogen. The oxygen is removed by combining it with copper (gauze) in the hard glass tube (*c*), which is heated by the combustion furnace (*b*). Before reaching the combustion tube, however, the air has to pass through the bottles (*ee*) containing a concentrated solution of potassium hydroxide to take out the carbon dioxide, and through the bottles (*dd*) containing concentrated sulphuric acid to remove the water vapor or moisture. The nitrogen collected in (*a*) is purer than that obtained by method shown in Fig. 54.

155. Water Vapor of the Air. — Some water vapor, derived from evaporation, is always present in the air; the amount usually increases with the temperature; thus warm breezes blowing over bodies of water are moist. When cooled, the vapor may condense as fog or rain. The air in desert regions though warm is dry, because the air before

being warmed has passed over a cool, mountainous region and has deposited its moisture.

The amount of water in the air, relative to the amount necessary to saturate the air under given conditions, is known as the *relative humidity*. This is high when the air is nearly saturated, and low when the air is very dry. If the air is warm and damp, it is sultry and uncomfortable; when the air is half saturated, it is comfortable; when the air is cool and damp, it is chilly and disagreeable.

156. Carbon Dioxide and Nitrogen Cycles. — Carbon dioxide is always present in the air, though in a very small proportion. In normal outdoor air about 4 parts in 10,000, or four-hundredths of 1 per cent, are present. The proportion may rise as high as 1 per cent in a crowded room from the exhalations of the people present. Carbon dioxide is continually given off to the air in the exhalations of animals and in combustion, but as it is taken up from the air by plants, the amount in the air remains practically constant. The very small percentage of carbon dioxide in the air furnishes all the carbon needed for the growth of plants.

The oxygen in the air is removed by animals and replaced by plant life; thus the plant and animal life preserve the balance, maintaining the atmosphere at a constant composition.

The nitrogen removed from the air, to form soluble compounds in the soil, is taken up by plants and converted into proteids. These proteids are the source of the protoplasm of animals. These unstable proteids break up both during the life of the plants and animals and after their death, and the nitrogen finally makes its way back to the air.

157. Other Constituents of the Air. — Other materials are found in small amounts, argon and helium (inert gases about 1%), traces of ammonia, sulphur compounds, and fine dust particles, which depend on local conditions and which often produce climatic effects. These dust particles include a great variety of materials — steel, stone, soil, and coal dust. The organic particles include pollen grains and spores of plants, germs and bacteria of disease, which are always present, shreds of various fabrics, as cotton and woollen cloth, and dried bits of refuse of all sorts.

THE INERT GASES.

158. Discovery of Argon. — The discovery and investigation of the inert gases in the air have afforded one of the most brilliant and interesting chapters in the history of chemistry. In 1892 Rayleigh, an English scientist, noticed that nitrogen from the air was a trifle heavier than that obtained from nitrogen compounds. This meant that the supposedly pure nitrogen from the air contained some gas, heavier than nitrogen, which had remained undetected despite the careful study of the atmosphere for more than a century.

A small amount of the hitherto unknown gas was obtained by Ramsay, an English chemist, who passed nitrogen from the air over heated magnesium which combined with the nitrogen, forming magnesium nitride, a yellowish solid. This method yielded but a trace of the new gas, and a better way was soon devised by Lord Rayleigh. Even this, however, was slow and required many precautions to secure a very small sample of the new material.

The new substance was found to constitute about 1% of

the air. It was one-fourth heavier than oxygen and over one-third heavier than nitrogen. All attempts to make the gas enter into chemical combination failed, and hence it was given the name *argon*, signifying inactive.

159. Isolation of the Other Inert Gases.— Certain irregularities in the properties of argon led Rayleigh and Ramsay to suspect that this new gas was not itself pure. By means of liquid air the argon obtained from the atmosphere was liquefied, and, at the low temperatures obtained, repeated processes of fractional evaporation and liquefaction were carried on. The argon was found to contain minute amounts of other inert gases. Two of these could be separated only by using the extremely low temperature possible with liquid hydrogen. Three of the new inert gases were given names which bring to mind the long, baffling search for them. *Neon* means new; *xenon*, stranger; and *krypton*, hidden. Besides these three gases a trace of helium was found. This element was formerly supposed to exist only in the sun.

160. Properties.— Neon, xenon, and krypton closely resemble argon, but each was found to have its *peculiar spectrum* and all except neon a very low but *definite boiling-point*. Thus they were elements and formed a very closely related group with argon. Certain considerations have led us to believe that all these elements contain but one atom to the molecule. Their inertness with respect to chemical combination explains why no compounds containing them are known, and why they were overlooked until recently.

161. Helium.— In 1869 Lockyer noticed some lines in the sun's spectrum which did not correspond with those

of any other element known on earth. This element was concluded to exist in considerable quantities in the sun. In 1895 Ramsay, in searching for sources of argon, examined the gases given off by certain rare minerals, as cleveite, when heated. In some cases a gas was obtained which gave a spectrum identical with that of the supposed element in the sun, and hence was given the name *helium*. The new element has since been obtained from the waters of certain mineral springs and exists in minute quantities in the atmosphere.

Helium is a very light gas, being only twice as heavy as hydrogen. Its properties resemble those of argon, and it is therefore classed with the other inert gases.

Recent researches have proved that helium results from the decomposition of radium, which was thought to be an element.

Summary.

Nitrogen constitutes the larger part of the air. It is a constituent of protoplasm and of proteids, hence is essential to vital processes.

It is prepared by

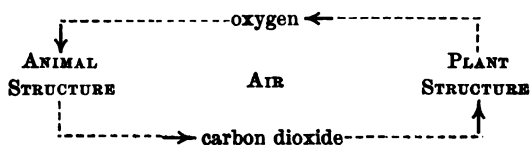
- (1) the oxidation of ammonium compounds ;
- (2) removing the oxygen from the air by phosphorus; this is sufficiently pure for ordinary use.

One liter of nitrogen weighs 1.26 grams. Its atomic weight is 14. The nitrogen molecule contains 2 atoms (N_2).

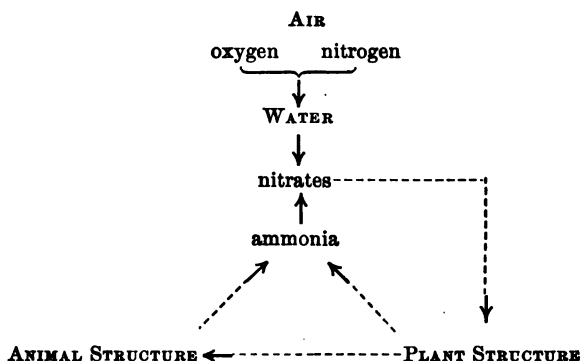
Nitrogen is generally inert ; under electric stress it reacts tardily with oxygen and with hydrogen. A few bacteria are capable of assimilating it.

Air is essentially nitrogen, oxygen, and argon, with varying amounts of water vapor, carbon dioxide, and compounds of nitrogen and sulphur. Nearly all the constituents of the air are produced by and used in vital processes.

CARBON OXYGEN CYCLE.



NITROGEN CYCLE.



The amount of the air is so enormous that local conditions have little or no appreciable effect on its composition. The important factor determining the composition is the balance maintained between plant and animal life.

The variation in composition indicates that air is merely a mixture. Chemical reactions are always accompanied by thermal changes.

Exercises.

1. Why are so few mineral compounds of nitrogen found in nature?
2. How was it shown that the material in the air, formerly known as nitrogen, was not a pure substance?

3. Under what influences does nitrogen react?
4. What chemical reactions take place in the air during a thunderstorm?
5. From what sources are the principal constituents of the air continually derived? By what means are they removed? Why is the composition of the air so nearly constant all over the earth?
6. What is the weight of air over a city lot 25×100 ft.? How much of it is oxygen?

CHAPTER XX.

NITROGEN COMPOUNDS.

AMMONIA.

162. Natural Formation. — The most important constituent of all living organisms is protoplasm, a complex substance containing nitrogen, carbon, hydrogen, oxygen, and other elements. When a plant or animal dies and decomposition sets in, the protoplasm breaks up very quickly, yielding simpler compounds. The nitrogen unites with the hydrogen to form the gas ammonia, the molecule of which contains one atom of nitrogen and three of hydrogen. Its formula, therefore, is NH_3 . Its characteristic odor can often be noted in the vicinity of heaps of decomposing animal or vegetable refuse.

163. Preparation. — Ammonia is obtained commercially as one of the products of the distillation of coal, in the manufacture of coal gas (Fig. 56). Soft coal is heated in iron retorts at an intense heat. Moisture, volatile matter, and gases are driven off, coke remaining in the retort. The gases are cooled in pipes, and coal-tar condenses. **Commercial** Then the gases are passed into a "scrubber" **method.** where they come in contact with water, and here the ammonia dissolves. The gases pass on to be further purified from sulphur compounds by passing through calcium and iron oxides in the purifier, previous to distribution as illuminating gas. The water containing ammonia com-

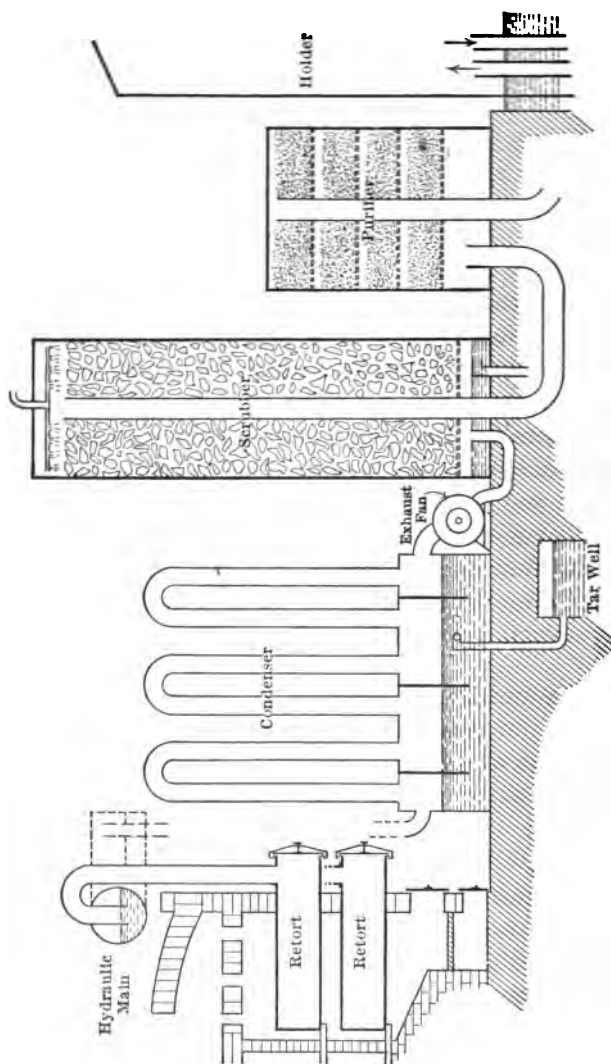
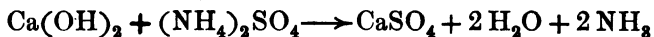


Fig. 56. Manufacture of coal gas by destructive distillation.

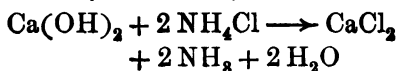
pounds is boiled with milk of lime, and the expelled ammonia is mixed with sulphuric acid; tarry materials are separated, and the solution of ammonium sulphate is evaporated and crystallized.

The dried, crystallized ammonium sulphate is mixed with slaked lime in an iron retort and heated. Ammonia gas and water are given off, and calcium sulphate remains:

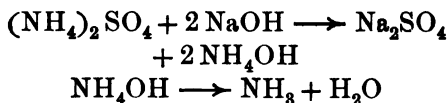


The ammonia is dissolved in water, forming ammonia water, or spirits of hartshorn, or it may be dried by passing through quicklime (CaO) and compressed in tanks.

In the laboratory, ammonia is usually prepared (Fig. 57) by heating ammonium chloride (sal ammoniac) with calcium hydroxide (slaked lime):



In this preparation any ammonium salt can be substituted for ammonium chloride, and any non-volatile base for the calcium hydroxide. A typical reaction probably proceeds as follows:



That is, ammonium hydroxide is first formed and breaks up at once into ammonia and water. Since ammonia is a gas, a volatile product can be formed as a result of the reaction between ammonium salts and bases. This is analogous to the fact that many acids are formed by the action of

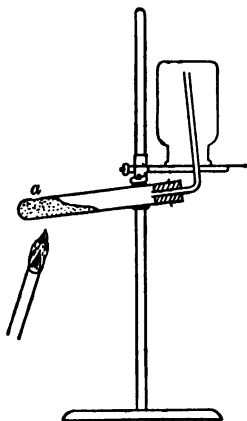
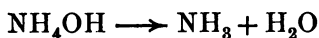


Fig. 57.

sulphuric acid upon their salts, because they have lower boiling-points than sulphuric acid.

Ammonia can also be obtained by warming a strong ammonium hydroxide solution :



164. Physical Properties.—Ammonia is a colorless gas with peculiar odor, lighter than air, and exceedingly soluble in water. At 0° C. one volume of water will hold in solution over 1000 volumes of the gas; at ordinary temperatures about 700 volumes. This solution is known as ammonia water, or ammonium hydroxide. On heating or on standing exposed to air, it gives off ammonia.

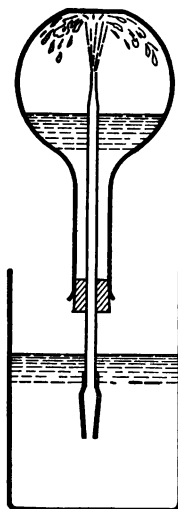
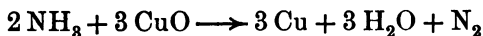


Fig. 58.

The great solubility of this gas is strikingly shown by the "ammonia fountain" (Fig. 58). A flask is filled with dry ammonia, and inverted over water. As soon as the clip (not shown in the figure) is removed from the rubber tubing, the water rushes in as the gas rapidly dissolves.

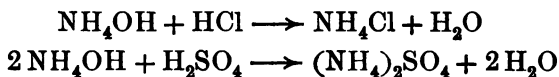
The gas is easily liquefied; at ordinary temperatures a pressure of 4.5 atmospheres is needed.

165. Chemical Properties.—Pure, dry ammonia is not an active substance; it is not readily combustible in air, but can be burned in oxygen. When ammonia is passed over heated copper oxide, water and nitrogen are obtained:



The most important chemical property of ammonia is

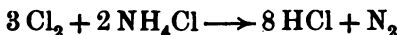
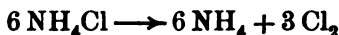
the *basic character of its water solution*. This solution, which is often incorrectly called ammonia, turns red litmus blue, neutralizes acids, and conducts electricity; it behaves like the solution of a base. When this solution is neutralized with hydrochloric acid, a salt is formed whose composition is represented by the formula NH_4Cl , and similar salts are formed with other acids:



We may assume, therefore, the existence of NH_4^+ ions and OH^- ions in the solution of ammonia. The group NH_4 is known as the ammonium radical. The solution, then, contains ammonium hydroxide, NH_4OH . **Ammonium radical.** There are a large number of ammonium salts, but ammonium has never been obtained in a free state.

Ammonium salts react similarly to the compounds of sodium and potassium, and they may be considered as substances in which the group of atoms NH_4 (ammonium radical) takes the same part as an atom of hydrogen or potassium. Thus as potassium chloride dissociates into K^+ and Cl^- ions, ammonium chloride, NH_4Cl , dissociates into NH_4^+ and Cl^- ions.

If an electric current is passed through a solution of ammonium chloride, we might expect to obtain ammonium and chlorine, since these are the ions formed. The chlorine, however, liberated at the anode reacts with the ammonium salt present in the solution, forming hydrochloric acid and nitrogen. At the cathode the NH_4^+ ion, on discharging, decomposes into ammonia and hydrogen, the ammonia dissolving in the water. The equations for the electrolysis are:



Thus by electrolysis we get one part of nitrogen and three parts of hydrogen.

166. Uses. — The most important uses of ammonia are as a refrigerating agent and for the preparation of ammonia water. When a gas is liquefied, heat is liberated, and when the liquid returns to the gaseous state, heat is absorbed. In the manufacture of artificial ice (Fig. 59), ammonia is

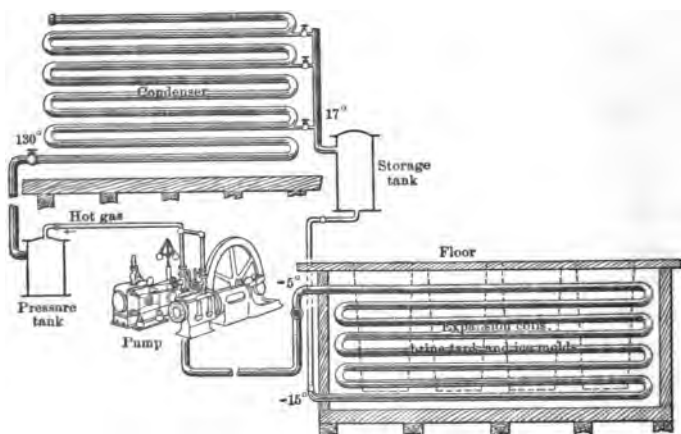


Fig. 59. Refrigerating plant.

liquefied by being compressed by powerful pumps; then the liquid ammonia is cooled by passing cold water over the pipes containing it. The liquid ammonia is distributed through pipes, where it evaporates rapidly. The gas is drawn back by the pump, condensed to a liquid, and used again. The pipes in which the evaporation takes

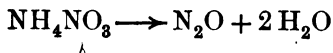
place are immersed in a strong salt solution, which, by furnishing heat for evaporation, is cooled to a point below the freezing-point of water. Cans of water are placed in the cooled brine, and the water is frozen in from 24 to 36 hours. Cold-storage rooms may be kept cool by distributing the cold brine to the apartments to be cooled, where it is passed through coils near the ceiling.

The value of ammonia water as a cleansing agent is due to its ability to dissolve grease. Its basic properties also give it a use in the laboratory, whenever a volatile alkali is desirable. Large quantities of ammonia are used in the manufacture of sodium carbonate by the Solvay process.

OXIDES OF NITROGEN.

Nitrogen combines with oxygen in five proportions, corresponding to the formulas: N_2O , nitrous oxide; NO , nitric oxide; N_2O_3 , nitrous anhydride; NO_2 , nitrogen peroxide; N_2O_5 , nitric anhydride.

167. Nitrous Oxide.—Nitrous oxide (N_2O), laughing gas, is prepared by heating ammonium nitrate (Fig. 60):

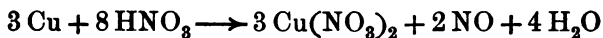


The nitrate melts and soon begins to decompose with effervescence. The heat must be carefully regulated or an explosion may occur. The nitrous oxide is a colorless gas with a slightly sweet taste; inhaled, it produces unconsciousness; for this purpose it is used in minor surgical operations. It was the first of modern anesthetics and was discovered by Sir Humphry Davy.

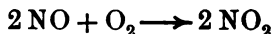
Nitrous oxide supports combustion almost as well as oxygen, but, unlike oxygen, it does not react with nitric

oxide or support the combustion of sulphur which is not burning vigorously.

168. Nitric Oxide.—Nitric oxide is a colorless gas; it is generally formed in the action of dilute nitric acid with metals. In the laboratory copper and nitric acid are used:



It does not support combustion, being more stable than nitrous oxide, but readily combines with oxygen, forming nitrogen peroxide, with a slight rise of temperature:



This action makes it useful as a catalytic agent in one process for the manufacture of sulphuric acid.

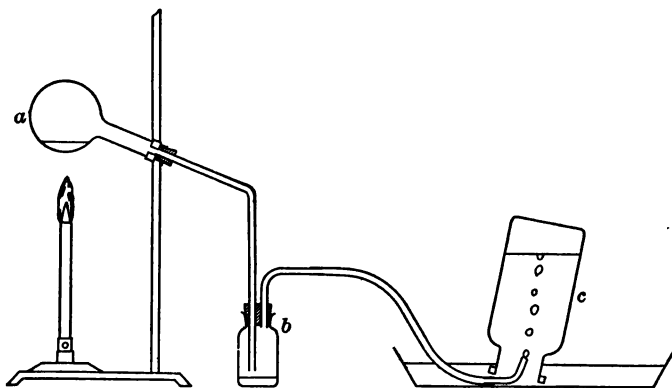
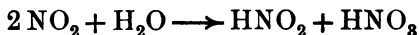


Fig. 60. Preparation of nitrous oxide.

a, flask containing melted ammonium nitrate; *b*, catch bottle for water formed;
c, collecting bottle.

169. Nitrogen Peroxide.—Nitrogen peroxide, NO_2 , is a heavy red-brown gas of disagreeable odor. It is formed immediately whenever nitric oxide is brought in contact

with oxygen or with air (Fig. 61). It dissolves in water, the solution has an acid reaction and contains nitrous and nitric acids:



Thus the fumes from nitric acid, containing oxides of nitrogen, form nitric acid with water, and cause the corrosion usually observed on metal objects near which nitric acid is kept.

Nitrogen peroxide is readily liquefied and solidified, the liquid being yellow and the solid colorless. When the liquid vaporizes, the vapor given off at the boiling-point is light brown and grows darker as the temperature rises. Vapor density determinations indicate that vapor given off has a composition represented by the formula N_2O_4 , part of the molecules of which *immediately* dissociate into NO_2 molecules, so that the light-colored gas is a mixture of the two oxides. As the temperature rises, more molecules dissociate, and the dark gas at high temperatures is chiefly NO_2 . These changes are represented by the equation:

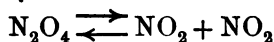
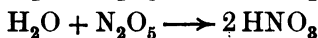
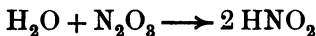


Fig. 61. Nitric oxide.
a, closed; b, open to air.

170. Other Oxides. — Nitrogen trioxide (N_2O_3) and nitrogen pentoxide (N_2O_5) are unstable substances of no particular importance. They unite with water, forming acids:



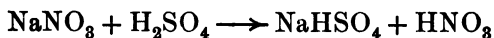
Hence the trioxide is termed nitrous anhydride and the pentoxide is known as nitric anhydride.

NITRIC ACID.

Nitric acid was known to alchemists, who called it *aqua fortis* (strong water), because of the great chemical activity it displays. They prepared it by heating a mixture of potassium nitrate, copper sulphate, and potassium aluminum sulphate. The last two of these substances contain water of crystallization, and from this came the hydrogen which the acid contains.

171. Preparation. — Both commercially and in the laboratory, nitric acid is prepared by heating a mixture of concentrated sulphuric acid and sodium nitrate (Fig. 62). The latter substance is found in considerable quantities in certain parts of Chile and in the western United States. Other nitrates might be used; for instance, potassium nitrate, which is also found in nature, though in much smaller quantity than sodium nitrate.

The reaction may proceed in two stages. The first reaction is:



If there is an excess of acid, the reaction does not proceed beyond this point. If, on the other hand, there is an excess of sodium nitrate, the sodium hydrogen sulphate that is formed in the first action reacts at a higher

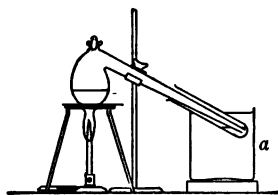
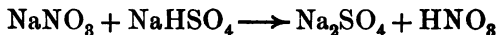
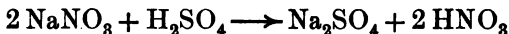


Fig. 62.

temperature with more sodium nitrate, according to the equation:



Writing one equation to show the final results of the two stages of the reaction, we have:



Since the second action requires a higher temperature than the first, and since nitric acid undergoes considerable decomposition at the higher temperature, it is customary to use sulphuric acid in excess to insure the first reaction. Sulphuric acid is used in this operation for the reason that its boiling-point is higher than that of nitric acid. Very few acids could be substituted for sulphuric acid because most of them have too low boiling-points. In the laboratory preparation of nitric acid, the distilled acid is usually collected in a test-tube or other receiver, kept cool by water in a battery jar (*a*, Fig. 62).

Nitric acid is an important article of commerce; so that the reaction that has been described is carried out on a large scale. Iron retorts are used, and the acid is condensed and collected in a series of earthenware vessels.

172. Physical Properties. — Nitric acid is a colorless liquid at ordinary temperatures, boiling, if free from water, at 86° C. The diluted acid has a higher boiling point, varying with the dilution. A mixture that contains 68% of this acid boils constantly at 120°.

As it is ordinarily prepared, nitric acid contains considerable water and is colored yellow by the presence of dissolved oxides of nitrogen, which result from the decomposition of the acid by the heat used in its preparation. It is usual to distil the acid in an apparatus in which the

pressure is less than that of the atmosphere. In this way the distillation can be carried on at a lower temperature and the undesirable decomposition is avoided.

173. Chemical Properties. — The chemical behavior of nitric acid is very interesting. Generally its action is not a simple one. This is because it possesses two distinct chemical characteristics, both of which it displays in a marked degree.

First, it is a very strong acid. This is because it is highly dissociated into ions when dissolved in water, even in concentrated solution. The hydrogen ions, being present in large numbers, produce all the actions that are characteristic of acids, such as the formation of salts with bases and the transference of the electric charge of the hydrogen ion to form metallic ions when the acid is brought in contact with a metal.

Second, nitric acid is a powerful oxidizing agent. This can be shown in a number of ways: charcoal can be made to burn in nitric acid; horsehair will take fire if put into the gaseous substance; both the coloring matter and fabric of cotton or woollen goods are quickly destroyed by it.

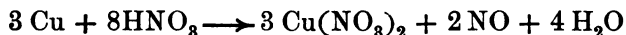
When nitric acid does oxidizing work, it is itself reduced. There are various reduction products of the acid. **Reduction products.** The product formed depends on a number of conditions, particularly on the temperature and the degree of dilution of the acid. In any case there are several reduction products, though usually one is found in excess of the others. If the acid is moderately dilute and acts at ordinary temperatures, the reduction product is commonly nitric oxide. From concentrated nitric acid a large quantity of nitrogen peroxide is always obtained. From very dilute acid the reduction product may be

nitrous oxide, hydrogen, or even ammonia. Thus we see that the more dilute the acid, the farther the reduction is carried. This does not mean that the more dilute acid is the stronger oxidizing agent; on the contrary, it is because the concentrated acid is such a powerful oxidizing agent that the lower reduction products cannot escape from the acid without being themselves oxidized to a certain extent.

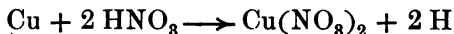
As we should expect from its being so strong an oxidizing agent, nitric acid is a rather unstable substance, tending to give up part of its oxygen to form more stable substances. It will do this under the influence of light, or more readily if some oxidizable substance is present.

174. Action with Metals.—Nitric acid acts with many of the metals, but owing to its dual chemical character, it does not act on them in the same way that other acids do. Hydrogen is seldom evolved by the action of nitric acid on metals. The gases that are given off are the reduction products of nitric acid.

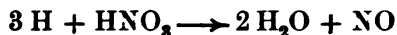
The action of moderately dilute nitric acid on copper can be taken as a type of its action on the heavy metals, as silver, mercury, and lead. Experiment shows that the products of this action are copper nitrate, nitric oxide, and water :



This equation represents the results of an action that takes place in two stages. It is probable that, as a result of the first stage of the action, there is a tendency to liberate hydrogen, according to the equation :



But the nascent hydrogen is at once oxidized by nitric acid :



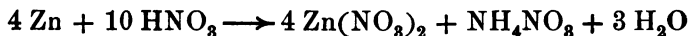
As a final result of these actions we get the products shown in the first equation.

The balancing of such an equation as this, involving oxidation and reduction, is a somewhat difficult matter. It will probably be found convenient to remember the numbers 3 and 8 in this reaction.

If concentrated nitric acid acts on copper, nitrogen peroxide is formed in considerable quantity, as well as some nitric oxide :



If very dilute nitric acid acts on zinc, or metals like it, the nitrogen of the acid is reduced to ammonia, which then combines with more of the acid, forming ammonium nitrate :

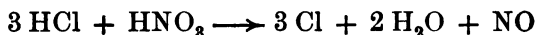


Nitric acid does not act on platinum.

175. Uses. — Nitric acid dissolves silver, but does not act on gold ; hence it is sometimes used to separate these two metals. The chief uses of nitric acid depend upon its ability to form unstable salts with organic bases (compounds containing hydrogen and carbon). Two of these products are nitroglycerine and guncotton. Celluloid is a mixture of guncotton and camphor.

Aqua regia is a mixture of nitric and hydrochloric acids. It dissolves gold and platinum. The fact that the mixture of the acids does what neither acting alone can do, is explained by the liberation of nascent chlorine by the inter-

action of the two acids. The hydrogen of the hydrochloric acid is oxidized by the nitric acid:

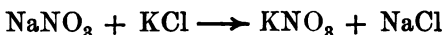


Nitric acid is also extensively used in the manufacture of many dyes and drugs.

NITRATES. -

176. Sodium and Potassium Nitrates.—The salts formed by the replacement of the hydrogen of nitric acid are called nitrates. The nitrates of sodium and potassium are the only ones found in nature in any considerable quantity. Potassium nitrate, ordinary saltpeter, is manufactured in a manner analogous to that by which it is produced in nature. Excreted animal matter which contains nitrogen decomposes under the influence of certain minute organisms and bases, and has its nitrogen transformed into nitrates. As a result of this action potassium nitrate gathers around stables. The potassium carbonate that is involved in the action is taken from the soil.

Sodium nitrate is found in large quantities in Chile, from which fact it gets the name *Chile saltpeter*. Nitric acid is made from it. Because of its great abundance sodium nitrate is cheaper than potassium nitrate. The following reaction will take place in hot concentrated solution:



Advantage is taken of the fact to prepare the more expensive potassium nitrate (cf. p. 138).

One of its chief uses is for the manufacture of gunpowder (page 138). Sodium nitrate cannot be used for this purpose, because it is slightly deliquescent. Potassium nitrate is used as a preservative in the making of corned beef.

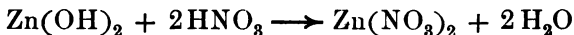
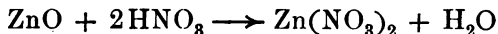
177. Preparation of Nitrates.—Nitrates, like the salts of the other common acids, can be made in several simple ways in the laboratory:

(a) By the action of nitric acid on metals:

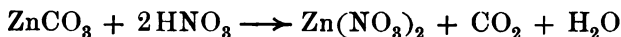


As has been pointed out, hydrogen is seldom a product in the action of nitric acid on metals.

(b) By the action of nitric acid on oxides or hydroxides of metals:



(c) By the action of nitric acid on salts that give volatile products with this acid:



Nitrates cannot be prepared by precipitation, because nitrates of all metals are soluble in water. This fact also prevents the use of a precipitation method as a test for a nitrate.

178. Test for Nitrates.—The test for the NO_3 ion depends upon the oxidizing power of the NO_3 group. The substance to be tested is mixed with a solution of ferrous sulphate. Concentrated sulphuric acid is then added, so as to form a layer below the mixed solution. Nitric acid oxidizes ferrous sulphate, and, at the same time, nitric oxide, NO , is formed as a reduction product. This combines with some of the unchanged ferrous sulphate, producing a characteristic unstable compound (whose formula is probably $2\text{FeSO}_4 \cdot \text{NO}$), which appears as a dark brown coloration or ring at the line of contact of the heavier sulphuric acid and the mixed solution above (Fig. 63).

All nitrates are decomposed by heat. The sodium and

potassium salts, when thus treated, give up oxygen and are converted into nitrites. Other nitrates yield oxygen and nitrogen peroxide, and the oxide of a metal.

179. Nitrification. — Nitrogen compounds are invariably found in certain tissues of both plants and animals. The nitrogen which helps to form these compounds comes from the soil, since neither plants nor animals, with one exception about to be noted, can take nitrogen from the air. The problem how to maintain the supply of nitrogen compounds in the soil has been somewhat difficult to solve. The renewal takes place slowly, and the soils become infertile because of the lack of nitrogen compounds. The difficulty is usually overcome by manuring the fields, in which case the decomposing animal matter gives up its nitrogen to the soil as ammonia.



Fig. 63.

It has been recently discovered that certain bacteria, which are found in the tubercles on the roots of leguminous plants, such as peas and clover, have the power of taking nitrogen from the atmosphere and converting it into nitrates of bases found in the soil. This discovery has been of great importance in rendering productive soils which had remained infertile from the lack of nitrogen compounds. The process of converting nitrogen from air into nitric acid or nitrates is called nitrification. It is difficult to accomplish because of the inactive character of nitrogen. Nitrification is brought about, to a small extent,

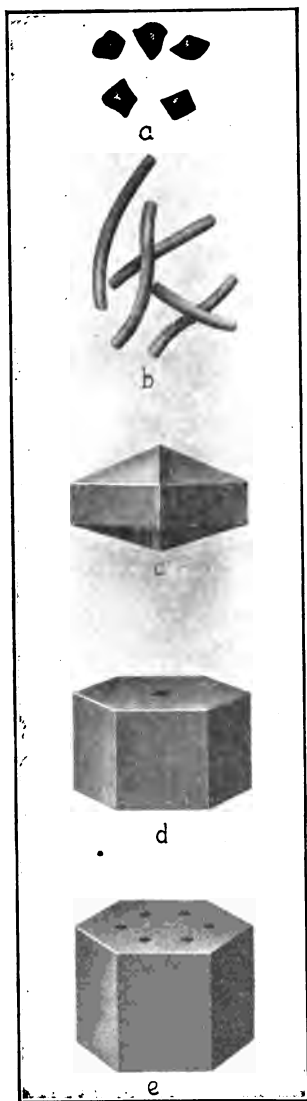
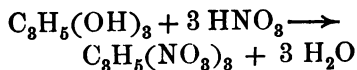


Fig. 64.

by passing electric sparks through air. The oxygen and nitrogen unite, forming nitrogen peroxide, which in turn forms nitric acid on dissolving in water. During a thunderstorm a certain amount of nitric acid is formed in this way. Attempts are now made to use these reactions for the manufacture of the acid.

180. Explosives.—Certain nitrogen compounds that contain carbon, oxygen, and hydrogen are so unstable that they decompose under the impulse of a slight shock, forming gaseous products. For this reason these compounds are powerful explosives. Nitroglycerine and guncotton are examples of this class of compounds. Nitroglycerine is made by treating glycerine, an organic base, with the mixture of nitric and sulphuric acids. The sulphuric acid serves to absorb the water that is formed by the reaction of the other two substances:



The nitroglycerine molecule is evidently a very unstable one that can rearrange itself into new and more stable molecules under the impulse of a slight shock. Dynamite is a mixture of some inert materials and nitroglycerine.

Guncotton (nitrocellulose) is made by treating cotton fibre (cellulose) with a mixture of nitric and sulphuric acids. Cellulose, like glycerine, is an organic base, and nitrocellulose is an unstable salt. One variety of smokeless powder is a special form of guncotton.

Some forms of explosives are shown on the opposite page: *a* is granular gunpowder; *b*, cordite; *c*, giant powder; *d*, brown prismatic powder; *e*, high explosive.

Summary.

Ammonia is formed in nature as a decomposition product from protoplasm.

It is obtained commercially as a by-product from the distillation of coal. It may be produced by the action of a base on an ammonium salt.

Ammonia is a gas with a pungent odor; its specific gravity, relative to hydrogen, is 8.5. It is very soluble in water, 1 liter of water at 15° dissolves 720 liters of ammonia.

The solution is basic and contains NH_4^+ and OH^- ions. It reacts with acids with the formation of ammonium salts.

Ammonia is used as a refrigerating agent, and in the preparation of sodium bicarbonate and of ammonia water.

Nitrogen forms five oxides.

Nitrous oxide, N_2O , is made by heating ammonium nitrate. It is a good supporter of combustion, and is used as an anesthetic ("laughing gas").

Nitric oxide, NO , is formed by the action of diluted nitric acid on metals. It unites with oxygen at ordinary temperatures, forming

nitrogen peroxide, NO_2 . This is a brown, poisonous gas, soluble in water.

Nitrous anhydride, N_2O_3 , and *nitric anhydride*, N_2O_5 , are unimportant.

Nitric acid is prepared by the reaction between sulphuric acid and a nitrate.

When pure, it is a colorless liquid, with a specific gravity of 1.53.

It is a powerful oxidizing agent, and when it reacts with metals, the hydrogen is oxidized to water and nitrogen oxides are liberated. A mixture of nitric and hydrochloric acid is *aqua regia*; this furnishes nascent chlorine.

Nitric acid is used in the preparation of nitrates and explosives.

The *nitrates* of sodium and potassium are the most important. Nitrates may be prepared by the action of nitric acid on:

- (1) metals;
- (2) oxides or hydroxides;
- (3) salts yielding volatile products.

Potassium nitrate is used in gunpowder and as a meat preservative; sodium nitrate as a fertilizer and for the production of potassium nitrate.

Nitrogen compounds are formed in the soils by bacteria, which cause the nitrogen of the air to enter into combination.

Many nitrogen compounds are used in *explosives*. Nitroglycerine and guncotton are made by the action of nitric acid on glycerine and cotton respectively. Dynamite is a mixture of inert materials with nitroglycerine.

Exercises.

1. How many liters of ammonia can be obtained by the action of lime on 50 grams of ammonium chloride?
2. Why is ammonia called "spirits of hartshorn"? why the volatile alkali?
3. What method would you use to get a few cubic centimeters of ammonia gas for use in the laboratory?

4. Explain what is meant by the ammonium theory.
5. Show how the nitrogen oxides illustrate the law of multiple proportions.
6. By what tests would you distinguish between oxygen and nitrous oxide?
7. What volume of air would convert 100 c.c. of nitric oxide, NO, into nitrogen peroxide, NO_2 ?
8. Compare nitric acid with sulphuric acid and with hydrochloric acid in regard to its action with metals.
9. Explain the natural formation of (a) ammonia, (b) nitric acid, (c) nitrates.
10. Why is nitric acid a better solvent than hydrochloric acid for silver, mercury, and lead?
11. What is *aqua fortis*? *aqua regia*? *sal ammoniac*?
12. Upon what properties of nitric acid do most of its uses depend? Illustrate.
13. How would you test an unknown substance for the nitrate ion? for the ammonium ion?
14. Explain the significance of the statement, "No life without nitrogen."
15. State the substances and conditions necessary to yield each of the following products from nitrogen compounds: oxygen, hydrogen, nitric oxide, nitrogen peroxide.
16. Why has it become necessary to devote much attention to the artificial production of fertilizers containing nitrogen?

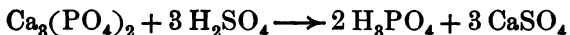
CHAPTER XXI.

ELEMENTS OF THE NITROGEN GROUP.

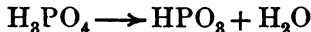
PHOSPHORUS.

181. Phosphorus, like nitrogen, is found in compounds associated with all living matter, in the protoplasm and bony structure of animals. A few, but widely distributed, minerals contain it, and most of these seem to have been derived from organic sources. Phosphorus was discovered in 1669 by Brand, an alchemist of Hamburg, while distilling urine in the course of his attempts to find the philosopher's stone. Scheele, the Swedish chemist, prepared it from bones in 1771.

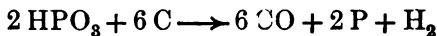
182. Preparation. — Phosphorus is prepared from bone-ash or other phosphates. The phosphate is ground and mixed in a vat with warm sulphuric acid, forming phosphoric acid and calcium sulphate:



The insoluble calcium sulphate is removed from the solution by filtering through coke. The phosphoric acid solution is concentrated, and absorbed in sawdust or coke, and dried:

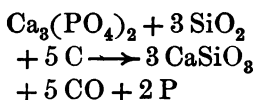


The dry carbonaceous mass is then distilled in clay retorts (Fig. 65) at a high temperature, phosphorus, hydrogen, and carbon monoxide being produced:



The phosphorus vapor is condensed in water and solidifies on cooling.

The electric furnace is used in a recent method for making phosphorus. The phosphate is mixed with fine sand and coke or coal and fed into an electric furnace. The non-volatile product, calcium silicate, settles to the bottom of the furnace, while the phosphorus vapor and carbon monoxide are passed into water and collected :



To purify the phosphorus, it is again distilled or filtered through bone-ash and then run into cylindrical moulds.

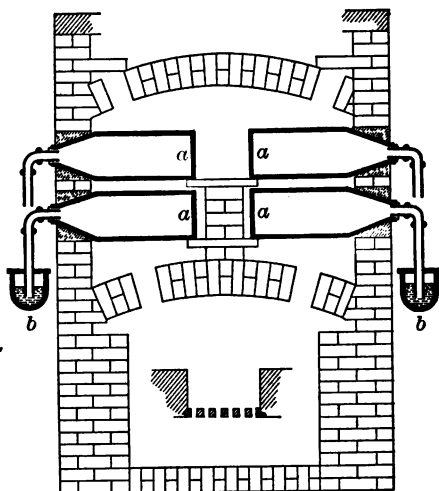


Fig. 65. Phosphorus distillation.

a, retorts; *b*, condensing vessels.

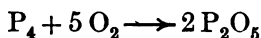
183. Physical Properties.—Phosphorus,

like sulphur, occurs in several allotropic forms. Prepared by the methods given above, it is ordinary or yellow phosphorus, a straw-colored, translucent solid, about as hard as beeswax, with a peculiar odor, due in part to ozone formed by its action on the oxygen of the air. It melts easily in water, but does not dissolve. In carbon disulphide, however, it is readily soluble.

Heated in a closed vessel to about 250° C., it becomes *red phosphorus*, which is red brown in color, opaque, and odor-

less. Red phosphorus is not easily ignited and does not dissolve in carbon disulphide. The red form is more dense and more stable than the yellow form. Red phosphorus can be converted into the yellow by distillation.

184. Chemical Properties. — Yellow phosphorus takes fire at 35°, burning with a brilliant flame and forming dense fumes of the oxide:



In moist air it glows and slowly oxidizes. The ease with which it burns makes it a very dangerous material. Yellow phosphorus is always kept under water.

Burns produced by phosphorus are very painful and difficult to heal. It is very poisonous; the vapor inhaled by workmen in the factories produces an incurable disease, characterized by ulceration of the jawbones.

Phosphorus combines readily with chlorine, iodine, and sulphur. Red phosphorus is less active than yellow; it burns with more difficulty, evolving less heat. All its actions indicate that the red variety has less energy than the yellow. Heat is evolved in the conversion of the yellow to the red, so that the red is the more stable form.

185. Uses. — A little phosphorus is used in medicine and in vermin poisons, but the larger part is consumed in the manufacture of matches. A common friction match consists of a stick of soft wood, tipped with sulphur, paraffin, or other easily combustible material, and a head composed of an oxidizing material, — as potassium chlorate or lead oxide, — phosphorus and glue, with coloring matter. The stick is dipped by machinery into melted paraffin which soaks into the wood, water-proofing it. Then it is dipped into a paste of the other materials and dried. The glue

protects the phosphorus from the air, but on rubbing, sufficient heat is generated to ignite the phosphorus in contact with the oxidizing material. This combustion will raise the temperature sufficiently to ignite the paraffin, and the burning of this will bring the wood to its kindling temperature.

As such matches are poisonous and very easily ignited, they are prohibited in many places and replaced by *safety matches*, the head of which consists of glue, antimony sulphide, and an oxidizing agent. The box against which they are rubbed has a surface of red phosphorus and powdered glass and glue. As the head of the match is soft, it will rub off on a rough surface and not burn, but it will usually ignite on a hard smooth surface, like glass or a slate blackboard.

186. Compounds. — Phosphorus, like nitrogen, forms several oxides and acids. Phosphoric oxide, P_2O_5 , is formed when phosphorus burns with a sufficient supply of air or oxygen. It is a white solid, which combines energetically with water, forming phosphoric acid.

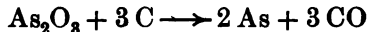
Phosphorus oxide, P_2O_3 , forms when phosphorus burns with a limited supply of oxygen. This white solid combines with water, forming phosphorous acid.

Phosphoric acid, H_3PO_4 , has several salts of common occurrence: ordinary sodium phosphate, Na_2HPO_4 , used in medicine; calcium phosphate, $Ca_3(PO_4)_2$, the principal mineral constituent of the bones; calcium acid phosphate, $CaH_4(PO_4)_2$, used in baking powder and fertilizers.

ARSENIC.

187. Arsenic is generally found in nature combined with sulphur, associated with iron and copper. The ore

is roasted, forming arsenious oxide, which is then reduced with carbon:



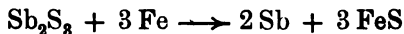
188. Properties. — Arsenic is a brittle, steel-gray, crystalline solid, with a metallic lustre, and tarnishes rapidly in the air. It volatilizes without melting at the ordinary atmospheric pressure and has an odor like garlic. It burns with a bluish flame, forming the oxide, As_2O_3 . In its physical properties, arsenic resembles the metals, but in its actions, it resembles the non-metals, especially phosphorus.

189. Uses. — Arsenic is added to lead in the manufacture of shot. The melted metal in a strainer or collander is dropped from a height into water. The arsenic lowers the melting-point of the lead and makes it more fluid, so that the shot becomes spherical before cooling. The arsenic also makes the shot harder than pure lead.

190. Compounds. — *Arsenious oxide*, As_2O_3 , is a white crystalline powder, slightly soluble in water, and, like all compounds of arsenic, poisonous. It is used in the manufacture of certain colors, also in medicine, and as a poison. *Arsenic sulphides*, realgar, As_2S_2 , and orpiment, As_2S_3 , are used as pigments. Paris green is a copper and arsenic compound used as pigment and as insecticide.

ANTIMONY.

191. Antimony is found combined with sulphur. It is prepared in a manner analogous to that for arsenic, or by heating the sulphide with iron:



192. Properties and Uses.—Antimony is a handsome, silver-white, crystalline, brittle solid, with a pronounced metallic lustre. It does not tarnish in air, but when heated in the air, burns, forming the oxide, Sb_2O_3 . As it does not change in air, it is used to cover other materials, as brass and lead alloys. *Antimony black* is finely powdered metal used to coat plaster casts imitating metal. Antimony alloys are usually hard. Britannia metal and pewter contain copper, tin, and antimony. Babbitt metal and other anti-friction alloys generally contain antimony.

Lead contracts on solidifying; an alloy of antimony and lead expands on solidifying and is hard. This alloy is used for type metal.

BISMUTH.

193. Properties and Uses.—Bismuth resembles antimony, but is more metallic. It has a red tinge, is brittle, crystalline, heavy, and tarnishes slowly in moist air.

Bismuth alloys are remarkable for their low melting-points. Bismuth melts at 270°C . The two most common alloys, Wood's metal and Rose's metal, have the following composition:

	WOOD'S METAL.	ROSE'S METAL.
Bismuth	50.0 %	82.0 %
Tin	12.5 %	9.0 %
Cadmium	12.5 %	. . .
Lead	25.0 %	9.0 %
Melting-points	65°C .	94°C .

Such easily melted alloys are extensively used: as fuses in electric connections, in fire alarms, in safety plugs, in boilers, and in automatic sprinklers in buildings. When

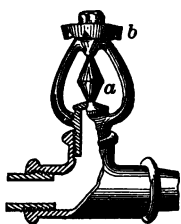


Fig. 66.

the fusible plug of a sprinkler (Fig. 66, *a*) melts, the water rushes out from the main and strikes a cap *b*, scattering the water in all directions. A piece of Wood's metal is sometimes placed in the gas-pipe where it enters the building, so that in case of fire the alloy will melt and stop the flow of gas.

194. Comparison of the Nitrogen Group.

	ATOMIC WEIGHT.	MELTING-POINT.	HYDRIDES.	OXIDES.	ACIDS.
Nitrogen	14	-210°	NH ₃	N ₂ O, NO, N ₂ O ₃ NO ₂ , N ₂ O ₅	Strong acid HNO ₃ HNO ₂
Phosphorus	31	44°	PH ₃	P ₂ O ₃ , P ₂ O ₅	H ₃ PO ₃ , H ₃ PO ₄ Weak acid
Arsenic	75	185°	AsH ₃	As ₂ O ₃ , As ₂ O ₅	H ₃ AsO ₃ , H ₃ AsO ₄
Antimony	120	630°	SbH ₃	Sb ₂ O ₃ , Sb ₂ O ₅	H ₃ SbO ₄
Bismuth	208	270°		Bi ₂ O ₃	Bi(OH) ₃ , Base

Summary.

Phosphorus exists in two allotropic forms. Both varieties, especially the yellow, have a great tendency to unite with oxygen. It also reacts readily with other non-metals.

Phosphorus is extracted from bone-ash.

Phosphorus is chiefly used for making matches.

Arsenic, though a non-metal, shows some of the characteristics of metals. It alloys with other metals and is used to make shot hard. Some of its compounds are valuable as paints.

Antimony shows the characteristics of both metals and non-metals. It is a constituent of type metal and other alloys.

Bismuth is a metal used in many alloys. These alloys generally have low melting-points.

The *elements in this group* resemble each other in properties to a considerable degree. It is approximately true that in going through the group, a given property changes steadily in one direction as the atomic weights increase. Thus nitrogen is a colorless gas; phosphorus is a waxlike solid; arsenic is a dark gray solid with something of the appearance of a metal; antimony has a distinctly metallic appearance; bismuth is a metal. Their respective specific gravities are: 0.97,* 1.8, 5.7, 6.7, 9.7.

The elements of the family form many compounds similar in character and formula. All except bismuth form compounds of the type XH_3 , where X stands for the symbol of any element in the family. There are two oxides, X_2O_3 and X_2O_5 , which are the anhydrides of the acids HXO_2 and HXO_3 respectively. In the cases of phosphorus, arsenic and antimony, the acid formulas are H_3XO_3 and H_3XO_4 , showing the addition of three molecules of water to the anhydride instead of one.

Exercises.

1. What is the per cent of phosphorus in calcium phosphate of the composition $\text{Ca}_3(\text{PO}_4)_2$?
2. What weight of oxygen would be used in combining with 0.5 gram of phosphorus? What would be the volume of the oxygen at standard conditions?
3. What weight of phosphorus would be necessary to remove the oxygen from 10 liters of air (measured at standard conditions)?
4. Why is yellow phosphorus always covered with water in the vessels in which it is kept?
5. Why do matches ignite on being rubbed?

* Air = 1; the other specific gravities refer to water.

CHAPTER XXII.

THE HALOGENS.

The elements fluorine, chlorine, bromine, and iodine are called *halogens* (salt formers), because they unite directly with a large number of metallic elements to form salts.

BROMINE.

195. Occurrence. — Bromine was discovered in 1826 by Ballard, who separated it from the mother-liquor of sea-salt.

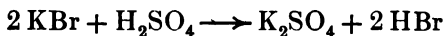
Large deposits of crude salt, impure sodium chloride, occur in the states of Michigan, West Virginia, Ohio, and Pennsylvania. Magnesium bromide and sodium bromide are two of the substances mixed with the sodium chloride. When the brines from the deposits mentioned are evaporated, nearly all of the sodium chloride crystallizes out before the magnesium salts begin to separate in an appreciable quantity. The liquid remaining, after a portion of the substances contained in the original solution has crystallized, is known by the technical term of mother-liquor. The compounds of magnesium remaining in the mother-liquor of salt works impart to it a bitter taste and cause it to be known as bittern. Extensive deposits of magnesium salts containing bromides are found in the almost inexhaustible salt beds at Stassfurt, Germany. The United States and Germany furnish a large percentage of all the bromine used.

196. Preparation.—Bromine can be prepared from the bromides by a method analogous to one of the methods described for the preparation of chlorine; namely, by heating a mixture of a bromide, manganese dioxide, and sulphuric acid (Fig. 67). Bromine, having a low boiling-point, passes off in the state of vapor, which can easily be liquefied by keeping the receiver cool.

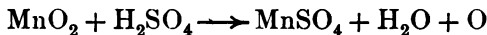
If a small quantity is made, the bromine vapor can be condensed in a test-tube partly filled with water (see *a* and *b* in Fig. 67).

The reaction may be considered as taking place in three steps.

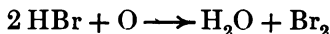
Sulphuric acid reacts with potassium bromide to produce potassium sulphate and hydrobromic acid:



When warm sulphuric acid is added to manganese dioxide, manganese sulphate, water, and oxygen are formed:



Nascent oxygen converts hydrobromic acid into water and bromine:



The equation for the complete reaction is:



Fig. 67. Preparation of bromine.

197. Physical Properties. — Bromine is a dark brownish-red liquid, about three times as dense as water. It is the only non-metallic element that, under ordinary conditions, exists in the state of a liquid. Bromine has an odor somewhat resembling that of chlorine; its name is derived from a Greek word meaning stench.

When a bottle of bromine is opened, the brownish-red vapor of bromine can be seen issuing from its mouth. If a few drops of bromine are poured into a large bottle filled with air, the vapor is seen first at the bottom of the bottle, and it diffuses slowly until it fills the bottle.

The vapor of bromine has a strong corrosive action on the mucous membrane. When it comes into contact with the eyes, the irritation is sufficient to cause a copious flow of tears. Great care should be taken not to inhale bromine vapor, and never to allow the bromine to come in contact with the skin. If bromine is inhaled, the irritation can be lessened by smelling of chloroform or alcohol. When bromine comes in contact with the skin, the injured part should be washed freely with water and then covered with a paste made by mixing sodium bicarbonate with water, or better with some oil, olive or cocoanut.

Bromine is somewhat soluble in water; the solution is called bromine water. Bromine is more soluble in aqueous solutions of the bromides than it is in pure water. It is very soluble in chloroform and in carbon disulphide.

198. Chemical Properties. — The chemical behavior of bromine very closely resembles that of chlorine. Bromine is, however, not so active an element as chlorine. We can illustrate this fact by comparing the action between chlorine and hydrogen with that between bromine and hydrogen. We have already seen that when a mixture of

chlorine and hydrogen is placed in the sunlight, the elements combine with explosive violence to form hydrogen chloride. Under similar conditions, bromine vapor and hydrogen enter into only a partial combination, without any *display* of energy. Aqueous solutions of bromine bleach many dyes, but the action is not as rapid as in the case of chlorine.

Bromine combines directly with a number of elements, as phosphorus, antimony, copper, and iron, forming bromides.

199. Uses.—Bromine is used in the manufacture of many organic compounds, especially certain of the aniline dyes, and in the preparation of bromides. Its water solution is used in the laboratory as an oxidizing agent.

HYDROBROMIC ACID.

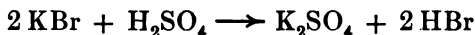
200. Preparation.—Hydrobromic acid can be prepared by the direct combination of bromine with hydrogen; the method is of no practical importance.

The addition of sulphuric acid to a bromide would probably appear to be a convenient method for the preparation of hydrobromic acid. A dilute solution of hydrobromic acid is prepared, on a commercial scale, by the reaction between diluted sulphuric acid and a solution of potassium bromide. The actual carrying-out of the process requires considerable time and most careful attention.

When concentrated sulphuric acid is added to potassium bromide, hydrogen bromide appears as a gas which fumes as soon as it comes in contact with the air. Other gases are formed at the same time; the odor of sulphur dioxide can generally be detected, and sometimes that of hydrogen sulphide. The products formed vary with the concentration of the sulphuric acid and the temperature at which

the reaction takes place. The more concentrated the sulphuric acid, and the higher the temperature, the less will be the amount of the hydrogen bromide produced.

Let us consider the reactions involved when sulphur dioxide is formed. Sulphuric acid reacts with potassium bromide to form potassium sulphate and hydrobromic acid:



The excess of concentrated sulphuric acid, however, oxidizes the hydrobromic acid, the result of the oxidization being water and bromine:



This is similar to the action of hot, concentrated sulphuric acid with copper (§ 139), in which a portion of the sulphuric acid is reduced to sulphur dioxide, and at the same time water is formed. The fact should be constantly kept in mind that when one substance is oxidized, some other substance is reduced.

If we use one equation to represent the formation of bromine and sulphur dioxide, by the method just considered, we obtain:



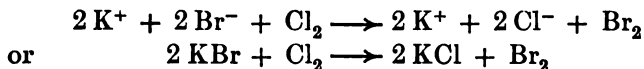
201. Properties. — Hydrobromic acid is a colorless gas, readily soluble in water, and its solution possesses the characteristic properties of a strong acid. Solutions of it are easily oxidized by the oxygen of the air, water and bromine resulting from the oxidation.

Dilute solutions of hydrobromic acid are used to some extent for medicine, and the bromides are an important series of salts.

Silver bromide separates as a yellowish white precipitate

when a solution of silver nitrate is added to a solution of a bromide. It is insoluble in nitric acid, slightly soluble in dilute ammonium hydroxide, and more readily soluble in concentrated ammonium hydroxide. These reactions are sometimes used as a test for a bromide.

202. Replacement of Bromine. — When chlorine is added to a solution of a bromide, free bromine appears and chlorine molecules pass into chlorine ions. The solution of potassium bromide contains potassium ions, bromine ions, and molecules of potassium bromide; the undissociated and dissociated potassium bromide being in equilibrium. As soon as chlorine is added, the bromine ions give their negative charge of electricity to the chlorine molecules, which then dissociate into ions. The bromine ions, having lost their charge of electricity, unite to form bromine molecules. As soon as some of the bromine ions pass out of solution, the equilibrium between the dissociated and the undissociated potassium bromide is destroyed, and more molecules of potassium bromide dissociate. If enough chlorine is added, all the bromine ions will finally appear as bromine molecules, and the solution will contain potassium ions, chlorine ions, molecules of potassium chloride, and molecules of bromine.



If there is too little bromine to be noticed in the presence of the yellow color produced by an excess of chlorine, its presence can be shown by adding a little chloroform or carbon disulphide, and shaking. Water and chloroform are not miscible (§ 37), and bromine is much more soluble in chloroform than it is in water. The bromine will be

distributed between the water and the chloroform in proportion to the ratio of its solubility in the two liquids.

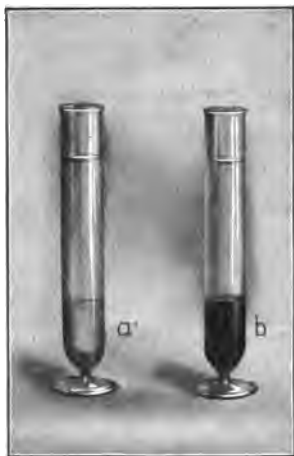


Fig. 68.

The solution of bromine in chloroform has a characteristic color; the bromine must be free, for combined bromine does not produce the characteristic color with chloroform, as is shown by shaking this liquid with a solution of potassium bromide (Fig. 68, *a*). Since a small quantity of chloroform can be used, to remove nearly all of the free bromine from a comparatively large quantity of water by shaking, the process is called *shaking out*.

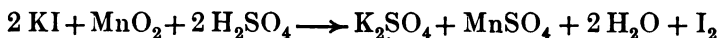
The liberation of bromine by chlorine, followed by shaking out with chloroform or carbon disulphide, is used as a test for bromine ions. If we add chlorine water to a solution of a bromide, and then shake with chloroform, the latter dissolves the free bromine, acquiring the characteristic reddish yellow coloration (Fig. 68, *b*).

IODINE.

203. Iodine was discovered by Courtois in 1812 while trying to prepare potassium nitrate from liquors obtained by washing the ashes of burnt seaweed. During his experiments Courtois observed the violet color of the vapor of iodine, but the properties of the element were first carefully studied by Gay-Lussac.

204. Preparation. — When seaweed (kelp) is burned at a low temperature, the ash contains considerable quantities of the iodides of potassium and sodium. As both of these salts are readily soluble in water, they can be separated from the insoluble portion of the ash by leaching or *lixiviation*; that is, by allowing water to slowly pass through the kelp.

Iodine is obtained from potassium iodide by a process analogous to that described for the preparation of bromine (§ 196); the iodide is warmed with manganese dioxide and sulphuric acid. Iodine passes off in the form of a vapor:



Large deposits of impure sodium nitrate are found in the dry region west of the Andes. Compounds of iodine occur in these deposits and most of the iodine used to-day is obtained from the mother-liquor of the sodium nitrate works.

205. Physical Properties. — Iodine is a steel-gray solid (Fig. 69), very slightly soluble in water, but readily soluble in alcohol, chloroform, carbon disulphide, and in aqueous solutions of potassium iodide. A solution of iodine in alcohol is called tincture of iodine. Solutions of iodine in chloroform and in carbon disulphide possess a characteristic violet color; iodine vapor has the

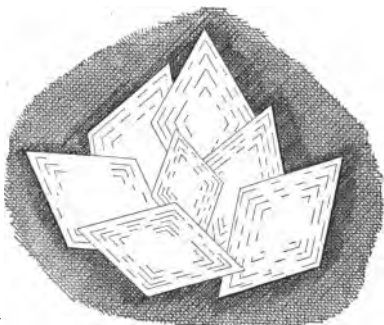
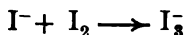


Fig. 69. Iodine crystals.

same color. Iodine vaporizes slowly at ordinary temperatures. When the solid is warmed, the change takes place rapidly, and the vapor on being cooled passes directly to the state of a solid. Such distillation of a solid is called *sublimation*, and may be used to purify solids that can be sublimed, as distillation is used to purify liquids.

The fact that iodine is more soluble in a solution of an iodide than in pure water is explained by the supposition that iodine ions combine with the iodine molecules to form triiodine ions:



The difference between the color of a solution of iodine in chloroform and the color of a solution of iodine in an aqueous solution of an iodide is due probably to the difference in the number of atoms in the particles of iodine entering the solution.

206. Chemical Properties. — Iodine unites directly with many elements to form iodides. The reactions are not as energetic as in the case of either chlorine or bromine. When a piece of yellow phosphorus and a piece of iodine are brought together, they combine to form an iodide without the application of heat (Fig. 70). Iodine and iron unite when heated.

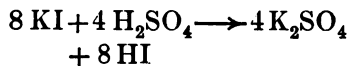
When a dilute solution of iodine is mixed with a dilute solution of starch paste, a characteristic blue color is produced. The reaction is made use of in testing for both iodine and starch.

Iodine is used in the manufacture of certain compounds which are used in medicine, in photography, and for dyeing.

HYDRIODIC ACID.

207. Preparation.—If concentrated sulphuric acid is added to an iodide, the odor of hydrogen sulphide is very noticeable. More hydrogen sulphide is produced than was formed when sulphuric acid was added to a bromide. This means that hydriodic acid is more easily oxidized (or is a better reducer) than hydrobromic acid.

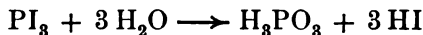
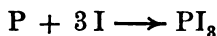
The formation of iodine by the action of sulphuric acid with potassium iodide can be represented by the following equations:



The equation for the complete reaction is:



Hydriodic acid can be readily prepared by the reaction of water with iodine and red phosphorus:



208. Iodides.—The iodides are important compounds, finding extensive use in medicine.

Both chlorine and bromine liberate iodine from the iodides. The presence of free iodine can be determined



Fig. 70.

by the starch test or by shaking out with chloroform or carbon disulphide.

THE HALOGENS AS A GROUP.

209. A comparison of the properties of the three halogens, chlorine, bromine, and iodine, leads to some interesting results:

NAME OF ELEMENT.	ATOMIC WEIGHT.	STATE.	SOLUBILITY IN ONE PART OF WATER AT 15° C.	HEAT OF FORMATION OF HYDROGEN COMP.	HEAT OF FORMATION OF POTASSIUM COMP.
Chlorine	35.5	Gas	2.4 vol.	22,000 cal.	104,300 cal.
Bromine	80	Liquid	0.032 pts.	8,400 cal.	95,100 cal.
Iodine	127	Solid	0.00015 pts.	-7,000 cal.	80,100 cal.

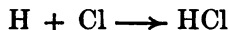
Chlorine, bromine, and iodine form a natural group of elements. The difference between the atomic weight of bromine and that of chlorine is nearly the same as the difference between the atomic weights of iodine and bromine. An examination of the table will show that the tabulated properties of the elements considered vary in degree with the atomic weights. Chlorine, bromine, and iodine very closely resemble each other in their chemical behavior. The chemical activity of bromine is less than that of chlorine and greater than that of iodine.

210. Heat of Formation.—When a chemical change occurs without the addition of energy, the substances resulting from the reaction usually contain less energy than the original constituents. Chemical energy has been transformed into some other kind of energy. In order to

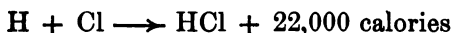
gain information in regard to chemical energy, it must be changed to some form of energy which can be measured. Heat is the form of energy most frequently considered in connection with chemical changes.

When elements unite to form chemical compounds, the heat evolved or absorbed is called the *heat of formation* of the compound in question. In measuring the heat of formation of any compound, weights of the substances equal to their reacting weights expressed in grams are considered, and the quantity of heat is commonly expressed in calories.

Hydrogen unites with chlorine to form hydrogen chloride. The simplest equation representing the reaction is:

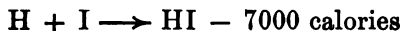


This shows that 1 gram of hydrogen unites with 35.5 grams of chlorine to form 36.5 grams of hydrogen chloride. During the combination, 22,000 calories of heat are evolved. The thermal equation for the formation of hydrogen chloride is:



The heat of formation of hydrogen chloride is 22,000 calories.

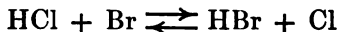
When hydrogen combines with iodine to form hydrogen iodide, an absorption of heat occurs. The thermal equation reads:



This shows that when 1 gram of hydrogen unites with 127 grams of iodine 7,000 calories of heat are absorbed. The heat of formation of hydrogen iodide is -7000 calories.

211. Relative Replacement and Heats of Formation. — Let us use the double arrow in the following equation to indi-

cate the two possible directions in which the reaction might proceed:



Would bromine replace chlorine or would the reverse be true? We may ask whether the displacement which would actually take place would not be in accordance with some general law governing chemical action. The following generalization has been developed from the study of the heat effects of many chemical changes.

When a chemical reaction takes place without the addition of heat from an external source, those substances which have the greatest heat of formation will tend to form.

The heat of formation of hydrogen bromide is 8400 calories; that of hydrogen chloride is 22,000 calories. Thus more heat is liberated when hydrogen unites with chlorine than is liberated when hydrogen combines with bromine. We should therefore expect chlorine to liberate bromine from hydrogen bromide. Chlorine does liberate bromine from hydrogen bromide. Chlorine and bromine liberate iodine from hydrogen iodide, as the heats of formation of hydrogen chloride, bromide, and iodide would lead us to expect. A study of the heats of formation of chemical compounds has been of value in the prediction of chemical reactions.

It should be remembered that heat is not the only form of energy into which chemical energy is converted, and in cases of solution in which chemical compounds are dissociated, the energy necessary to dissociate the compounds is an important factor in the thermal equation.

FLUORINE.

212. Activity. — Fluorine belongs to the halogen group, but does not so closely resemble the other members of the

group as they resemble each other. A consideration of fluorine has therefore been made to follow a study of the other members of the group.

Fluorine is an element of unusual chemical activity; few substances are not attacked by it. It cannot be isolated in the presence of water, as it unites with the hydrogen in the solution and liberates the oxygen. Furthermore, it cannot be prepared in glass vessels, as it reacts with the glass. The heats of formation of the fluorides are too great to permit of their being easily decomposed by heat. From the statements just made it will be seen that fluorine cannot be prepared by the methods generally employed in the preparation of the other halogens.

213. Preparation. — The problem of isolating pure fluorine puzzled chemists until 1886, when Moissan discovered that a solution of potassium fluoride in liquid hydrofluoric acid conducted the electric current.

The apparatus used by Moissan to carry on the electrolysis consisted of a U-tube made of an alloy of platinum and iridium, carrying electrodes composed of the same material, which were insulated from the U-tube by calcium fluoride stoppers (Fig. 71).

The solution of potassium fluoride in hydrofluoric acid was placed in the U-tube and kept at a temperature near -23°C . during the electrolysis. Moissan subsequently found that a U-tube made of copper could be substituted for the one composed of the expensive alloy mentioned.

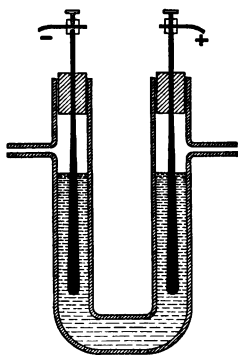


Fig. 71.

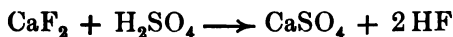
During the electrolysis, fluorine is liberated at the anode and passes off through the side arm of the tube surrounding it. Hydrogen is liberated at the cathode. Potassium passes to the cathode, but, on giving up its electric charge, instantly unites with fluorine, forming potassium fluoride, which dissolves in the excess of hydrofluoric acid. The result of this electrolysis is that only the hydrofluoric acid is permanently decomposed.

214. Properties.—At ordinary temperatures fluorine is a nearly colorless gas, much more poisonous than chlorine. Liquid fluorine combines energetically with hydrogen, sulphur, phosphorus, arsenic, some other elements, and many compounds, showing that violent chemical action can take place at a very low temperature.

Under ordinary conditions, fluorine has a greater tendency to form compounds than any other element. Copper, when placed in fluorine becomes coated with an insoluble coating of copper fluoride. The fluorides of calcium, strontium, and barium are insoluble. Silver fluoride is soluble. Gold and platinum, which readily form compounds with nascent chlorine, are very slowly attacked by fluorine. No oxide of fluorine is known. It is interesting to compare the properties of fluorine just mentioned with those of chlorine, bromine, and iodine.

Two compounds of fluorine which occur in nature are of importance: calcium fluoride or fluor-spar, CaF_2 , and cryolite, $3\text{NaF} \cdot \text{AlF}_3$. Cryolite is used in the preparation of aluminum by the electrolytic process.

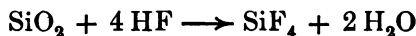
215. Hydrofluoric Acid.—Hydrofluoric acid is prepared by the action of sulphuric acid with fluor-spar:



The reaction is commonly carried on in a lead or platinum dish.

Pure hydrofluoric acid is a colorless liquid which fumes strongly in air. It dissolves readily in water and aqueous solutions of it are sold in wax bottles. Great care should be exercised in using this acid, as painful sores, difficult to heal, are produced when it comes in contact with the skin.

The chief use of hydrofluoric acid is in the etching of glass. Glass is composed of silicates, and hydrofluoric acid converts the silica, silicon dioxide, of the glass into a gas, silicon fluoride, and water:



Glass is prepared for etching by covering it with a coating of some substance which is not attacked by hydrofluoric acid, such as paraffin or a mixture of beeswax and rosin, and then removing the coating from the part to be etched. The etching is accomplished by subjecting the prepared piece to hydrofluoric acid vapor, or by



Fig. 72. Etching with hydrofluoric acid.

applying to it a water solution of the acid (Fig. 72). When the gas is used the surface of the etching is left dull, while with a water solution it is left glossy. Hydrofluoric acid is used in the finishing of cheap cut glass, and for the removal of sand from castings.

Summary.

Bromine, atomic weight, 80, resembles chlorine very closely. The chief points of difference are that it is a dark-colored liquid and that it is less active. In general, bromine reactions are like those of chlorine except for the difference in intensity.

Bromides are found in nature associated with chlorides. Bromine is prepared from bromides by a process exactly analogous to that used in the preparation of chlorine from sodium chloride. A mixture of a bromide and manganese dioxide is treated with concentrated sulphuric acid. The manganese dioxide acts as an oxidizing agent on the hydrobromic acid that is formed by the action of the sulphuric acid with the bromide.

Hydrobromic acid is formed by the action of moderately concentrated sulphuric acid with potassium bromide. There is a marked difference here from the action that occurs in the preparation of hydrochloric acid. The difference is due to the fact that the hydrobromic acid is less stable (*i.e.* has a less heat of formation) than hydrochloric acid. The secondary products formed in the case of hydrobromic acid are mainly sulphur dioxide and free bromine, resulting from the oxidizing action of the sulphuric acid.

Bromine and its compounds are not of great commercial importance. Bromides are used in medicine, and free bromine is used in the preparation of certain dyes.

Since bromides have smaller heats of formation than the corresponding chlorides, free *chlorine will displace bromine* from bromides. The presence of free bromine in solution may be detected by the color it imparts to carbon disulphide or chloroform.

Iodine, atomic weight, 127, is found as iodide in small quantities in the ashes of sea-plants, and associated with sodium and potassium compounds. It is a dark gray solid with the suggestion of a metallic appearance. In its chemical properties it is like chlorine and bromine, but it is less active than either. Thus we find that with these three elements, as the atomic weight increases, the

activity diminishes, and the elements lose something of their non-metallic character.

Iodine may be prepared by a process analogous to that used in the preparation of chlorine or bromine.

Hydriodic acid results from the action of moderately concentrated sulphuric acid with potassium iodide, but only a small part of the expected quantity is obtained. The heat of formation of hydriodic acid is so low that it is very readily oxidized by the sulphuric acid. Sulphur dioxide, free sulphur, hydrogen sulphide, water, and free iodine may all be formed in this secondary action.

Iodides have a less heat of formation than bromides. Consequently free *bromine will displace iodine* from iodides. Chlorine will do the same thing, even more readily.

Fluorine, atomic weight, 19, is the most intensely active element known. Hydrofluoric acid is a stable compound used in etching glass.

The four *halogens*, considered as a group, may be regarded as the most nearly perfect representative of a chemical family. The properties change in a very definite and regular way with the change in atomic weight.

Exercises.

1. Prepare a table of the halogens according to the following form:

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Element	Atomic weight	Compounds found in nature (Formulas)	Equations for the preparation of element	Physical properties
<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	
Chemical properties	Relative replacing power	Equations for the preparation of the hydrogen compound	Stability of the hydrogen compound	

2. Write equations for the preparation of potassium bromide by three different methods.

3. A solution contains potassium chloride and potassium bromide. How would you show the presence of the two halogens?

4. What weight of iodine could be obtained from 150 grams of potassium iodide? How much sulphuric acid would be needed for the action, assuming that the acid sulphate of potassium is produced?

5. Solutions of hydriodic acid become dark colored on standing. To what substance is the dark color probably due? Explain the action that produces it.

6. A solution of sodium bromide is treated with an excess of silver nitrate, and 0.65 gram of silver bromide is precipitated. What weight of sodium bromide was contained in the original solution?

7. Why should bottles of bromine water be kept in a dark place?

8. Write the equations representing the reactions of bromine with zinc, water, antimony, and hydrogen. Name the products in each case.

CHAPTER XXIII.

CARBON.

216. Unusual Character. — Carbon, though a non-metal, differs in several important respects from the other elements of its class. The chief difference is that it forms almost numberless compounds with hydrogen. These substances are called *hydrocarbons*. In addition to these, there are many compounds that are composed of carbon, hydrogen, and oxygen; others are known which contain in addition chlorine, bromine, iodine, nitrogen, or sulphur. There are so many of them that the branch of chemistry which deals with them has a special name, that of *organic chemistry*. The compounds of this sort that were first known were found only as products of animal or vegetable life; that is, of organized bodies—hence the term *organic*. It was formerly believed that such substances could not be made artificially, but to-day many of them are manufactured in large quantities. A very large number of organic compounds that are not known in nature have been made in the laboratory.

217. Importance of Carbon in Nature. — Every living thing, plant or animal, contains carbon in its tissues in the form of organic compounds. The higher plants always contain a large amount of cellulose, which is composed of carbon, hydrogen, and oxygen. The woody part, which furnishes the strength necessary to keep the plant erect, is cellulose. All plant fibres, such as cotton and hemp,

are composed of cellulose. Cotton fibre is the purest form of cellulose that is known.

The muscular tissue of animals is composed of a class of bodies known as proteids. They contain carbon, hydrogen, oxygen, and nitrogen, with a very small quantity of other elements. The fat of animals is composed of carbon, hydrogen, and oxygen. The starting material for the formation of all these complicated compounds is the carbon dioxide of the air. The green leaves of plants contain chlorophyl bodies, substances by which starch is made from carbon dioxide and water under the influence of sunlight as a source of the necessary energy. This synthesis has never been accomplished in the laboratory. The starch is converted in the plant into other compounds. These serve in turn as the food of animals, and furnish material for the building of animal tissues.

218. Occurrence.—It is apparent from what has been said that a very large number of compounds of carbon are found in the realm of organic nature. The element is also found in carbon dioxide of the atmosphere, and very abundantly in the carbonates of certain metals, especially calcium and magnesium. Marble and limestone are two different varieties of calcium carbonate. A considerable part of the earth's crust is made up of these materials.

In the uncombined form carbon is found as coal, graphite, and diamond.

219. Coal.—There are two chief forms of coal and several less important varieties. None of them is pure carbon. Anthracite or hard coal (Fig. 73, *d*) contains 90 % to 98 % of uncombined carbon. Bituminous or soft coal (Fig. 73, *c*) contains 60 % to 70 % carbon. The remain-

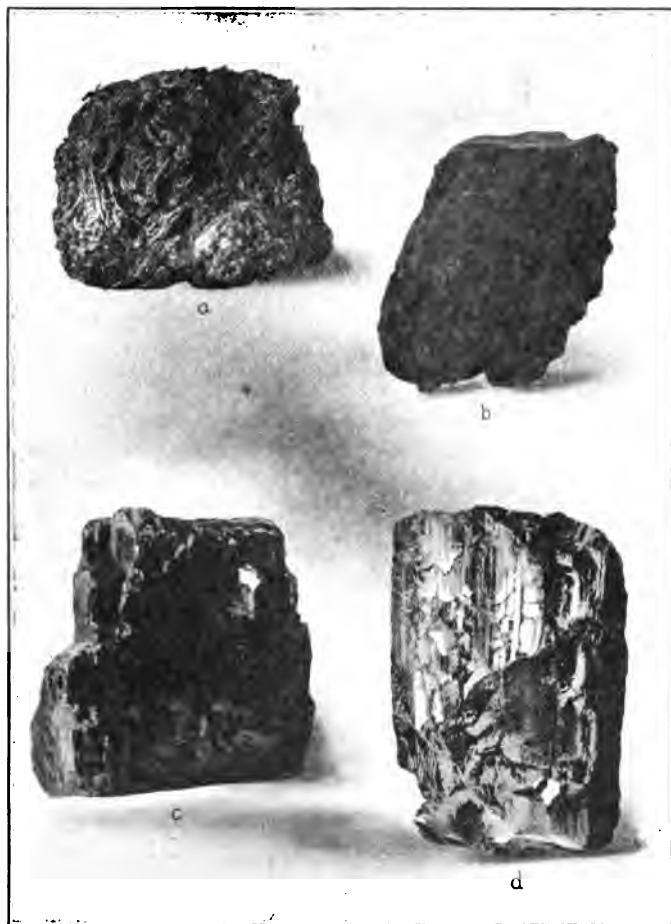


Fig. 73. Fuels:

a, peat; *b*, lignite; *c*, soft coal; *d*, anthracite.

ing 40 % to 30 % is chiefly hydrocarbons. These can be driven off as gases by heating the coal without access of air. This operation furnishes a means of making one kind of illuminating gas.

Coal is fossil vegetable matter. During a part of the earth's history, known in geology as the carboniferous period, vegetation flourished to a remarkable extent. Much of this vegetable matter was buried under beds of mud and sand. In this condition it underwent very slow partial decomposition. A large part of the hydrogen and oxygen was driven off, and the remainder, consisting of uncombined carbon, was left as coal. In anthracite coal the decomposition has proceeded further than in bituminous coal.

Some forms of coal contain even less uncombined carbon than does the bituminous variety. Cannel coal and lignite belong to this class. Lignite exhibits much of the structure of the wood from which it was derived (Fig. 73, *b*). Peat is moss or other loose vegetable matter that, to a slight extent, has undergone a change like that by which coal was formed (Fig 73, *a*).

OTHER COMMERCIAL FORMS OF CARBON.

220. Lampblack.—Lampblack, or soot, is practically pure carbon. It is best made by burning hydrocarbon oils with a limited supply of air. The operation is analogous to that which takes place when a kerosene lamp smokes. The hydrogen of the oil burns, but much of the carbon remains unburned because of the lack of oxygen. The unburned carbon is deposited as a soft, amorphous powder. Lampblack is used in making paint and printers' ink.

Large quantities of lampblack are made from natural gas by using machines of special design. One of these lampblack machines (Salsburgh patent) is shown in Figure 74.

The cast-iron disk (*D*), about four feet in diameter, is mounted on a hollow shaft. The burner (*G*) is made of one-inch gaspipe in which are placed lava tips about two inches apart. The burner is mounted close to the disk in such a position that the flames from the tip will be divided, half of the flame depositing a thin coating of soot, or lampblack, on the concave surface, and the other half of the flame depositing a thin coating on the convex surface of the disk.



Fig. 74. Manufacture of lampblack.

As the disk revolves slowly in the direction of the arrow, the scraper (*S*) removes the lampblack from the disk and the black powder falls through the hopper (*H*) to a spiral conveyor not shown in the cut. The conveyor delivers the lampblack to the bolters, where it is sifted and prepared for sacking.

The top of the disk is kept full of running water, which cools the disk and then empties into the hollow shaft. The disks are run in groups of fifteen in rooms kept closed so as to avoid draughts.

221. Wood Charcoal. — Wood charcoal is made by heating wood without access of air. To a certain extent this operation resembles the natural process by which coal was formed. The hydrogen, oxygen, nitrogen, and some of the carbon which the wood contains pass off in the form of various compounds. The operation is known as *destructive distillation* (Fig. 120, page 375). The charcoal which remains is uncrystallized in form, but it retains the cell structure of the wood from which it was formed. Charcoal is not pure carbon, as is shown by the fact that it leaves an ash on burning.

222. Boneblack. — Boneblack is a form of charcoal that is obtained by heating bones without access of air. Bones contain both mineral and animal matter. The animal matter, consisting of carbon compounds, is converted into charcoal by destructive distillation; the mineral matter, which is calcium phosphate, is separated from the charcoal by being dissolved in hydrochloric acid. Boneblack is extensively used for filtering purposes. It has the power of absorbing both coloring-matter and gases from solution. Other forms of carbon have the same property in a less degree. It is attributed to the porous character of charcoal. The most important use of boneblack is in the decolorization of sugar and oils.

223. Coke and Gas Carbon. — Coke is an amorphous form of carbon obtained by the destructive distillation of bituminous coal. It is obtained as a by-product in the manufacture of one kind of illuminating gas.

Gas carbon is found on the top and sides of iron retorts used for the destructive distillation of bituminous coal in the manufacture of illuminating gas. It differs from coke

in being nearly pure carbon ; coke leaves considerable ash on burning. Gas carbon is a fairly good conductor of electricity and is used for making the carbon rods for arc lights.

ALLOTROPIC FORMS.

224. Among all the varieties of carbon, three distinct allotropic forms are recognized. These are amorphous carbon, of which lampblack is the purest form ordinarily obtained, graphite, and diamond. The different varieties of charcoal, coal, and coke are impure forms of amorphous carbon.

The three allotropic forms can each be burned in oxygen, if raised to a sufficiently high temperature, with the formation of nothing but carbon dioxide. This fact proves that the three substances are different forms of the same element. They differ widely in physical properties and in the ease with which they burn.

225. Amorphous Carbon. — As the name implies, amorphous carbon is without crystalline structure. Its density is low; it is soft, and it does not conduct an electric current very well. These properties cannot be specified definitely because they vary according to the temperature to which the element has been subjected. Amorphous carbon burns with comparative ease.

226. Graphite. — Graphite is a crystalline form of carbon. There are a number of natural deposits of graphite, the best coming from Ceylon and Siberia. Graphite is now produced artificially by heating coke with a small percentage of iron in an electric furnace. The coke is converted into graphite, and the iron is vaporized. The crystals of graphite appear as minute scales or plates, which present

a very good sliding surface. To this property is due the use of graphite as a lubricant. It differs from other forms of carbon in being very soft, in conducting the electric current readily, and in having a very high kindling temperature. Like all forms of carbon, it has a very high melting-point. The refractory nature of graphite permits its use in crucibles for melting metals. Its resistance to heat and its conducting power cause it to be extensively used for the melting-pots and electrodes of electric furnaces. Graphite is also used for making lead pencils. The varying degrees of hardness in the pencil are secured by mixtures of graphite and clay.

227. Diamond. — Diamond, the third form, is also a crystallized variety of carbon. It is found as octahedral crystals, sometimes colorless and transparent, sometimes tinted or black. The diamond differs from the other allotropic forms in being extremely hard. It is the hardest substance found in nature. Like graphite, it burns only when heated to a high temperature. The use of diamonds as gems is due to their great rarity, and to the fact that light in passing through them is highly refracted so that a sparkling play of color results. This effect is heightened by cutting the surface of the stone into numerous facets. The value of a diamond depends largely on its color and its brilliancy. Black stones are used only for cutting instruments for use on hard materials.

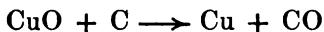
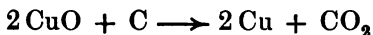
Microscopic diamonds have been made artificially. Carbon dissolves in melted iron. If such a solution is heated to a very high temperature, in an electric furnace, and then suddenly cooled in water or melted lead, the outer part of the iron solidifies first, producing an enormous

pressure on the still liquid interior part. The carbon, in separating from the cooling solution under this great pressure, takes the form of minute diamond crystals.

228. Chemical Properties.—The *physical properties* of carbon have been described in discussing the allotropic forms of the element.

None of the forms of carbon reacts with either acids or bases. They are all insoluble in ordinary solvents. Melted iron dissolves carbon to a certain extent.

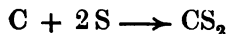
Carbon has a great tendency to unite with oxygen at high temperatures. It burns in the gas and also unites with the oxygen that is held in combination with other elements. On this account carbon makes an excellent reducing agent, and since it is cheap, it is the reducing agent most extensively used. The reaction of carbon with copper oxide illustrates this property. When the mixture is heated, metallic copper is produced; the other product is carbon dioxide or carbon monoxide, according to the relative amounts of the substances used:



Enormous quantities of coke are used in the reduction of metals, particularly iron, from their ores.

If a mixture of copper oxide and charcoal is heated in a test-tube (Fig. 75 *a*) and the gas led into lime water (Fig. 75 *b*), a white precipitate of calcium carbonate indicates the presence of carbon dioxide.

Carbon unites directly with only a few elements. If heated in the presence of sulphur vapor, carbon disulphide is produced:



In spite of the fact that carbon forms so many different compounds with hydrogen, it unites directly with this element only at the tempera-

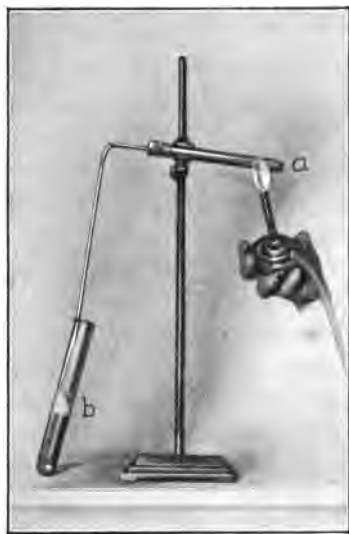
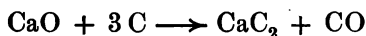


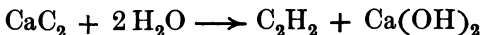
Fig. 75.

ture of an electric arc, and then very slowly. By using the high temperature of an electric furnace, carbon can be made to unite with many metals and some non-metals. The compounds made in this manner are called *carbides*.

229. Carbides and the Electric Furnace. — The intense heat of an electric furnace makes carbon react with lime (calcium oxide), and calcium carbide is formed:



Calcium carbide is used to prepare *acetylene*, a gas which makes an excellent illuminant. The gas is generated by the action of calcium carbide with water at ordinary temperatures:



Acetylene is used in bicycle and automobile lamps and in places where the gas supply of a city system is not available.

The electric furnace (Fig. 76) is a device by which a very high temperature is obtained by using a large arc between carbon terminals. The arc consists of carbon

vapor, which conducts the current over the gap between the carbons and the resistance is so great that much heat is developed. A temperature of about 3000° C. is obtained. The reactions that occur in the electric furnace are due to the high temperature. The electric current does not directly play any part in the reactions.

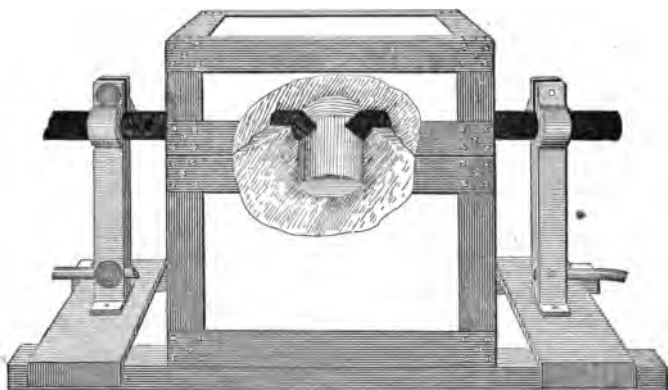
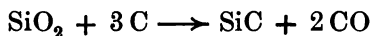


Fig. 76. Electric furnace.

Carborundum, silicon carbide, is made by heating sand, silicon dioxide, and carbon in an electric furnace (Fig. 87):



230. Uses. — The uses of carbon have been pointed out in the discussion of the properties of the element. Coal is the principal source of artificial heat. Anthracite is, in general, the most desirable kind of coal, because it burns with practically no flame and without the formation of soot. It burns, however, more slowly and gives a more uniform heat than does bituminous coal. Coke burns like anthracite coal and is sometimes used in its place. In warm countries charcoal is often the only fuel used.

Many metals are separated from their ores by the aid of coke as the reducing agent. The making of coke from bituminous coal for this purpose is an important industry. Iron is obtained in this way, usually by the reduction of hematite, ferric oxide. Enough coke is used to give carbon monoxide as the reduction product, and this gas is used in other parts of the plant as fuel.

Charcoal and boneblack are both used to remove gases and coloring-matter from solutions. Impure water is sometimes passed through charcoal filters for purification. This method, while it may suffice for the removal of impurities which can be seen or smelled, is not to be relied upon for the removal of disease germs.

231. Flame of Candle. — We have seen numerous cases of combustion or burning. When the fuel is a solid, particles of the fuel or of the ash are often heated to incandescence and glow. When a stream of gas burns, a flame is produced. This phenomenon can best be studied in the flame of a common candle.

When a light is applied to the tip of a candle wick, a flame appears and slowly spreads down the wick toward the candle and upward about twice the height of the wick. In a few moments the flame becomes constant in size and position (Fig. 77). Starting about one-eighth of an inch from the candle, the flame begins to be visible, rounded at the base and tapering to a sharp point above. It entirely encloses the wick except at the base and at the extreme tip.

If we examine the flame closely, we see four parts. The first is a *greenish blue portion of the base*, shaped much like the cup of an acorn. This follows the wick downward a short distance, and its upward extension is hidden by the

glare of light within. Second, above and within the first green portion we find, immediately surrounding the wick, a region dark, compared with the more brilliant part above, but in reality transparent and colorless, as is shown by placing an object behind it. This region tapers to a cone above and is termed the *non-luminous cone*. Covering the cone just mentioned is a bright cap known as the *luminous cone*. This is the third and most conspicuous region of the flame. Outside the luminous cone we can find the fourth region, which is the faint and scarcely visible blue *mantle*.

The candle is composed of a mixture of paraffin and stearic acid, both of which contain carbon and hydrogen. The upper portion of the candle, heated by the flame above, melts, so that the top becomes a cup holding a small portion of the melted fuel. This melted portion is drawn up the wick by capillarity, and vaporizing, forms the non-luminous cone immediately surrounding the wick. If we insert a tube into this portion of the flame, we can lead out a quantity of vapor which condenses to a solid similar to that composing the candle. If we extend a thin piece of wire across the flame, we find that it is not very warm near the wick; in fact the head of a match can be placed there without igniting. There is no combustion in this non-luminous cone since there is neither air nor sufficient heat.

As the vapor is carried upward by the draft it becomes mixed with air and combustion ensues, and this region of active burning is brilliant and hot, but not transparent.



Fig. 77.

If we place a piece of cold porcelain in this portion of the flame, or lead off some of the materials through a tube, we find a considerable portion of lampblack (carbon) and moisture. The carbon while in the luminous cone is heated to incandescence.

Since the combustible vapors are slowly mixed with air, the materials may move considerable distances from the wick before they meet sufficient oxygen to burn; hence when a large wick is used, the bulk of vapor makes an extensive region of flame. Indeed, the upper extremity is often so far removed that its temperature falls below the kindling temperature of the combustible materials. These escape unburned or the flame smokes.

In the outer portion of the flame the conditions are reversed, in that the air is in excess. Here the combustion is complete, but usually only a small amount of combustible material reaches this pale outer portion. This material, if drawn out by a tube, is found to be principally air mixed with products of combustion. The pale green cup below is similarly constituted; but from its position *below* the principal region of combustion and its nearness to the cool wick and candle, it is not so warm as the blue mantle *above*.

The wick is made of cotton and is proportioned to the quantity of material to be burned. The cool stream of liquid drawn up the wick protects it from burning, and, at the same time, prevents the flame extending down to the candle. As the candle material is vaporized, the wick chars somewhat but does not burn, since there is no oxygen in its immediate vicinity. In braiding the wick, one of the threads is drawn tighter than the others, so that the wick, when free from the candle stuff, is drawn over to one side of the flame. This braiding of the wick brings the tip into the outer zone of combustion, where it burns so far as

air is available, rotating as the candle shortens and practically maintaining a uniform length. This is why modern candles do not need to be trimmed.

232. Gas Flames. — In the ordinary gas flame the following four regions are clearly marked: the region of fuel, or non-luminous cone; the luminous cone, or region of luminosity; outside and lower regions of combustion with an excess of air. In a Bunsen burner we can adjust the proportions of gas and air so that there shall be no excess of either. Then the flame will appear to have two regions, a lower cone where no combustion is apparent and the cap above. The combustion is more rapid in that the fuel does not get far from the burner before burning. Therefore, the flame is smaller and *for this reason* hotter. It is not luminous, owing to the rapid and complete burning and to the dilution of the materials by the nitrogen.

In the ordinary flame, we find the position of maximum temperature somewhat above and outside the light-giving materials. A very large part of the energy passes off as heat and only a very small per cent is converted into light. If the solids giving light could be placed above or in the region of maximum temperature, they would evidently be hotter and give more light. Auer von Welsbach accomplished this by placing a mantle composed of a net of infusible and incombustible materials in the outer portion of the flame of a Bunsen burner. The materials are heated to incandescence and produce the brilliant light given by the Welsbach burner.

Summary.

Carbon is a non-metallic element, characterized by the *enormous number of compounds* it forms with the non-metallic elements, especially hydrogen, oxygen, and nitrogen.

Carbon is an *inert element at ordinary temperatures*; at higher temperatures it combines readily with oxygen and with a few other elements; at the temperature of the electric furnace it reacts with lime, forming calcium carbide.

Amorphous carbon, graphite, and diamond are the three *allotropic forms of carbon*. These allotropic forms differ widely in physical properties, but all yield the same product when burned in sufficient oxygen.

Carbon is found combined in the tissues of every living thing, in the carbon dioxide of the atmosphere and in metallic carbonates. Uncombined it occurs as coal, graphite, and diamond.

Anthracite coal is nearly all carbon; bituminous coal is about two-thirds carbon and one-third hydrocarbons; cannel coal and lignite are poor in uncombined carbon.

The *uses of the forms of carbon* are:

Coal, fuel and manufacture of illuminating gas;

Lampblack, paint and printers' ink;

Wood charcoal, fuel and filtering;

Boneblack, filtering and decolorizer of sugar and of oils;

Coke, fuel, ore reducer, and manufacture of water-gas;

Graphite, lead pencils, lubricant, crucibles, and electrodes for high temperatures;

Diamond, gem and abrasive.

The four portions of a *candle flame* are the greenish blue region at base, the non-luminous cone, the luminous cone, and the blue mantle. The ordinary gas flame has four similar portions, while that of the Bunsen burner appears to have but two—the lower cone and the surrounding conical cap above.

Exercises.

1. Wöhler is said to have broken down the barrier between organic and inorganic chemistry when, in 1828, he prepared from chemicals, urea, a waste product of the body. Why?

2. Why are the decomposition products of animal and vegetable matter so similar?

3. Tell how the carbon in your muscular tissue is indirectly derived from the air.

4. Why does soft coal make such a smoky fire?

5. Why is anthracite coal preferred for household use?

6. Explain why fence posts are sometimes charred at the end before being placed in the ground.

7. What properties of lampblack make it suitable for printers' ink?

8. What kind of carbon is used in batteries?

9. Write the equation for the chemical reaction when an excess of carbon is heated with zinc oxide, ZnO .

10. What three conditions are necessary for ordinary burning?

11. Why does water put out a fire?

12. If a taper is held over a gas burner, a flame may be maintained several inches above the burner without "striking back" to the burner. Explain.

13. Why does not the flame of a Bunsen burner extend down the tube to the base?

14. In working with compressed air it was found that combustible materials burn with more flame than usual. Explain.

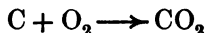
15. Why does the light increase with the pressure under the condition given in question 14?

16. Why is the flame of a Bunsen burner hotter with the holes open than when they are closed? Is the total heat increased?

CHAPTER XXIV.

OXIDES OF CARBON.

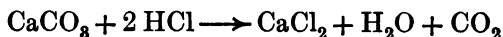
233. Natural Formation. — There are three very important sources of carbon dioxide: the decay of vegetable and animal matter; the oxidation constantly going on in animals, and to a much smaller extent in plants; the combustion of all ordinary fuels, such as wood, coal, and gas. These fuels consist largely of carbon; this, on burning, combines with oxygen, forming carbon dioxide:



Hence the gas is always present in the air, usually to the amount of four parts in ten thousand (§ 156). This percentage would be much higher were it not for the fact that plants are constantly taking it in, building the carbon into their tissues and returning the oxygen to the air. Natural waters also very commonly contain it; in some spring waters the gas is dissolved in such quantities that they are effervescent, that is, they give off gas in bubbles unless kept in tightly closed vessels. It is also given off by volcanoes and from other subterranean sources, and from fermenting liquids. It is found in mines, where it is known as *choke damp*.

234. Preparation. — Carbon dioxide is most conveniently prepared in a pure state by the action of an acid on a carbonate (Fig. 78). Calcium carbonate is generally used on account of its abundance, as marble, limestone, and chalk

consist almost entirely of this compound. Hydrochloric acid is commonly used in the laboratory on account of the solubility of calcium chloride which it forms. The equation representing the action is :



To remove any hydrochloric acid that may be carried over the gas is allowed to bubble through water. The gas is collected by downward displacement of air or over water.

235. Physical Properties. — Carbon dioxide is a colorless gas with little taste or odor. It is about one and one-half times as dense as air, so that it can be poured from one vessel to another like water. In wells, caves, or mines, carbon dioxide is often set free from soil or water, and if there is poor ventilation, it will accumulate.

It is soluble in water, which dissolves about its own volume at ordinary temperatures. Under increased pressure, water dissolves more of the gas; if the pressure is removed, the gas is slowly given off. Soda water is water into which carbon dioxide has been forced under pressure (60 to 150 lb.) and effervesces when drawn. Liquids bottled during fermentation, as champagne and kumiss, effervesce for a similar reason. The liquefied gas is also used like ammonia in refrigerating and ice-making processes, particularly on ocean vessels where ammonia might be dangerous.



Fig. 78. Preparation of carbon dioxide.

a, generator; *b*, collecting bottle.

236. Chemical Properties. — Carbon dioxide is chemically inactive toward most substances, being the product of the complete oxidation of carbon. It does not burn nor support combustion (Fig. 79). Burning potassium, sodium, and magnesium, however, will decompose it, uniting with the oxygen and setting the carbon free. The presence of a small percentage of carbon dioxide in the air extinguishes combustibles and causes death by suffocation. A candle will go out in air containing 4 % of the gas, and when a little larger amount is present, life is impossible.

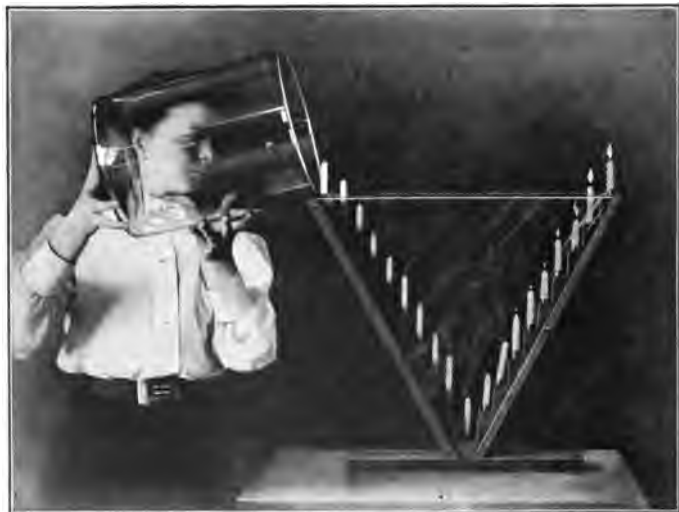
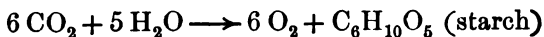


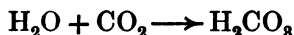
Fig. 79. Candles successively extinguished by pouring carbon dioxide into V-shaped trough.

The most important reaction of carbon dioxide is its decomposition, under the influence of light and chlorophyll, whereby oxygen is set free :

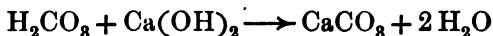


The water in this reaction comes up from the roots of the plant and the carbon dioxide comes from the air.

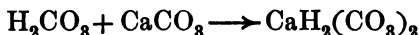
The solution of carbon dioxide has a slightly acid reaction and forms carbonates with bases. Carbonic acid, like ammonium hydroxide, has never been isolated, but the formation of carbonates indicates the presence of hydrogen ions and CO_3 ions. We may write the equation:



Carbon dioxide, then, passed into a solution of a base produces the corresponding carbonate. As calcium carbonate is insoluble, calcium hydroxide (lime-water) is used as a test for the presence of carbon dioxide. When carbon dioxide is first passed into lime-water, it becomes milky, and on standing a precipitate of calcium carbonate separates:

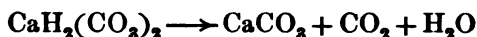


If the passage of carbon dioxide is continued, the precipitate dissolves. This is because it has been converted into calcium bicarbonate, which is soluble in water:



237. Hard Waters. — The solubility of calcium carbonate in water containing an excess of carbon dioxide explains the formation of one kind of *hard water*. In regions where limestone is abundant, the surface water, becoming charged with carbon dioxide from decay going on in the soil, dissolves some of the limestone, converting it into calcium bicarbonate. If an attempt is made to use soap with such water, it is found difficult to obtain a lather, as the dissolved limestone reacts with the soap to form an insoluble compound. By boiling hard water of this kind,

part of the carbon dioxide is driven off and the calcium bicarbonate is converted into calcium carbonate:



The carbon dioxide escapes and the calcium carbonate is precipitated. If the rocks contain magnesium carbonate, this may be converted into the bicarbonate and dissolved in the same way as with the calcium compound, and the water may be softened by the same means. Water containing such dissolved bicarbonates is called water of *temporary* hardness. Water of *permanent* hardness contains *sulphates* of calcium and magnesium and cannot be softened by boiling.

238. Uses. — Many uses of carbon dioxide have been alluded to. As an easily soluble, non-poisonous gas, it is extensively employed in the manufacture of beverages. Seltzer, vichy, and other mineral waters are produced artificially by charging solutions whose composition is similar to that of the original spring. Fire extinguishers (Fig. 80) often contain a device for generating carbon dioxide rapidly, as by mixing sulphuric acid (*b*) or alum solution with sodium carbonate (*a*). In chemical engines the pressure of the gas itself is sometimes used to throw a stream of water.

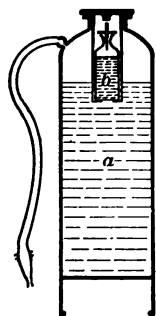
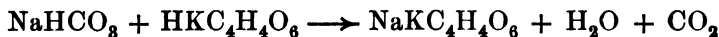


Fig. 80.

The raising of bread depends on the expansion of bubbles of carbon dioxide by heat, the carbon dioxide being generated by yeast or by the reaction of sodium bicarbonate (baking soda) and a material of acid reaction; for example, acid potassium tartrate (cream of tartar).



The compound, sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6$, is known as Rochelle salt.

CARBON MONOXIDE.

239. Preparation. — As carbon monoxide differs from carbon dioxide in containing one atom of oxygen instead of two, it can be prepared by the reduction of carbon dioxide. This is best accomplished by passing a current of carbon dioxide over carbon heated to redness in a hard glass or iron tube (Fig. 81). The carbon acts as a reducing agent:

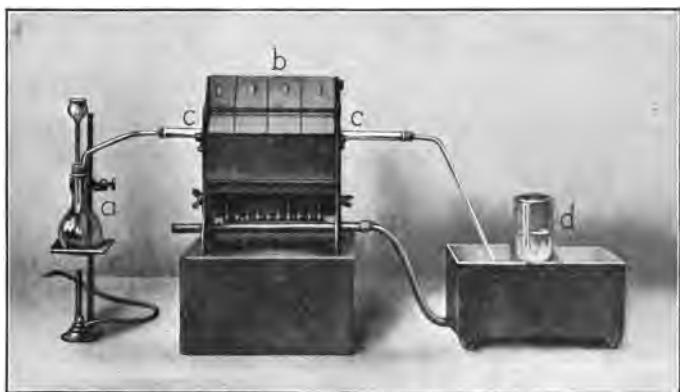
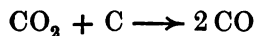


Fig. 81. Preparation of carbon monoxide.

a, carbon dioxide generator; *b*, combustion furnace; *c*, tube containing red-hot carbon;
d, collecting bottle.

This action takes place in a coal fire where the carbon dioxide, formed near the bottom, is reduced by the hot coal above to carbon monoxide, which may be seen burning at the top of the fire.

In the laboratory carbon monoxide is commonly made by the decomposition of oxalic acid (Fig. 82). This, heated with concentrated sulphuric acid, decomposes:



The purpose of the sulphuric acid is to extract the water formed in the decomposition of the oxalic acid. The carbon dioxide is removed by passing the gases through a concentrated potassium hydroxide solution.

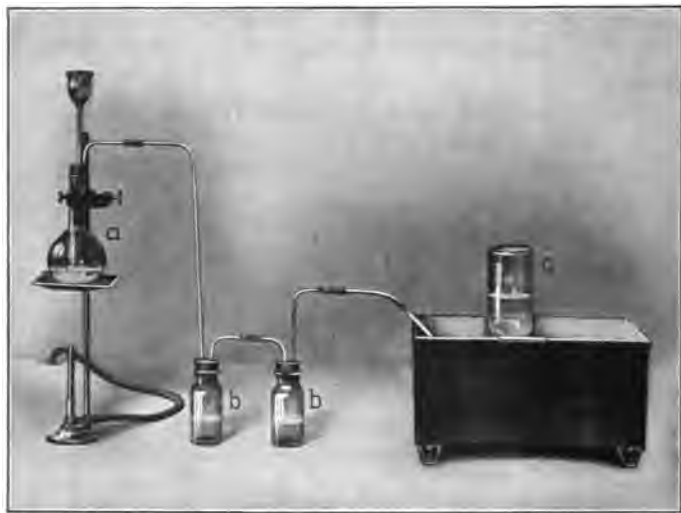


Fig. 82. Preparation of carbon monoxide.

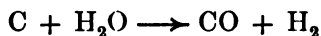
a, generator containing oxalic and concentrated sulphuric acid; *b*, bottles containing concentrated solution of potassium hydroxide; *c*, collecting bottle.

240. Physical Properties.—Carbon monoxide is a colorless gas with a slight odor. It is slightly lighter than air and is nearly insoluble in water. It is extremely poisonous, a very small percentage in the air causing headache, and a larger amount death.

Chemical Properties. — Under ordinary conditions the monoxide burns in air with a blue flame. If both the carbon monoxide and the air are dry, however, combustion does not take place. Carbon monoxide may act as a powerful reducing agent. The reduction of oxides of iron in the blast furnace is largely due to it. The heated carbon monoxide, formed by a blast of hot air forced through coke, diffuses through the furnace, and reacts with the iron oxide, producing carbon dioxide and metallic iron, which melts and runs to the bottom of the furnace.

Carbon monoxide prevents the oxygen of the air from uniting with the hæmoglobin of the red blood corpuscles, entering itself into combination with the hæmoglobin. It is because of this action that a comparatively small amount of the gas will cause death. The compound formed in the corpuscles has a brilliant red color, and is so stable that it can be detected in a body years after death. Carbon monoxide is the chief poison in illuminating gas and the gas escaping from stoves.

241. Uses. — The chief use of carbon monoxide is in *water gas*. This is produced by the reduction of steam by heated coal:



The process (Fig. 83) consists essentially in alternately forcing air and steam through incandescent anthracite coal or coke contained in an iron cylinder (*producer*). Air is forced through until combustion is vigorous. Then the air is shut off and the outlet of the chimney closed; superheated steam is next forced in. This reacts as we have seen above and the carbon monoxide and the hydrogen pass together into another cylinder (*carburetter*),

where the gas is mixed with the vapor of hydrocarbons. This mixture is thoroughly blended in the *superheater* and then goes through various purifiers (*scrubbers*) to the storage tank or holder. The object of the addition of the hydrocarbons is to give the mixture of hydrogen and carbon monoxide substances that will produce light in burning, as the original gases burn with non-luminous flames.

Carbon monoxide is the principal heat-giving constituent of another gas known as *producer gas*. This is made by forcing air over a bed of incandescent coke in a furnace of special form. Although producer gas contains about 63% of nitrogen, it is extensively used as a fuel on account of its cheapness, cleanliness, and the even temperature of its burning.

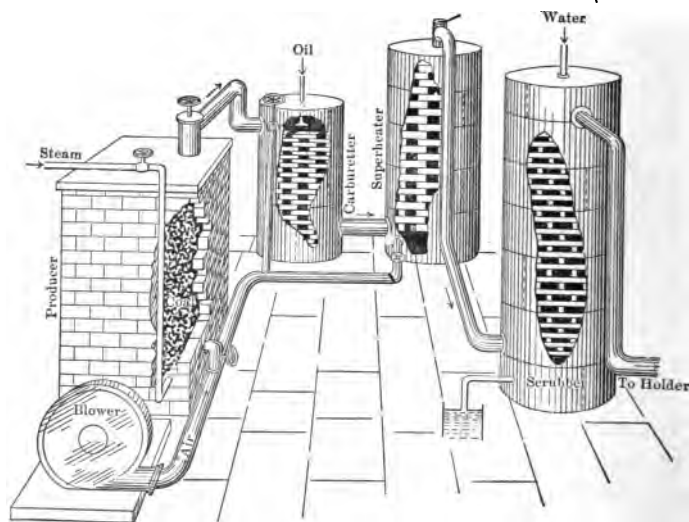


Fig. 83. Manufacture of water gas (diagrammatic).

Summary.

Carbon dioxide is formed in the vital processes of plants and animals and in ordinary combustion.

It is prepared commercially by the reaction of acids with carbonates.

Carbon dioxide is colorless, slightly soluble in water, and suffocating, but not poisonous.

One liter (standard conditions) weighs 1.98 grams.

It reacts with soluble bases, forming carbonates. Small quantities render lime-water turbid, excess of the dioxide causes the precipitate to dissolve. Such water is *temporarily hard*; boiling expels the excess of carbon dioxide, and the calcium carbonate again separates.

Carbon dioxide is used in charging beverages, in fire extinguishers, and in ice machines.

Carbon monoxide is formed by:

- (1) the incomplete combustion of carbon;
- (2) the reduction of the dioxide;
- (3) the reaction of steam and red-hot coal.

Carbon monoxide is lighter than air, has a slight smell, and is very poisonous. One liter (standard conditions) weighs 1.26 grams.

It burns with a pale blue flame, forming the dioxide.

Carbon monoxide is used as a fuel in producer gas, and is one of the constituents of water gas.

Exercises.

1. How can it be shown that there is carbon dioxide in the air?
2. Why is hydrochloric acid preferred to sulphuric acid in preparing large quantities of carbon dioxide from calcium carbonate?
3. Calculate how many liters of carbon dioxide, at standard

conditions, can be obtained by treating 45 grams of pure marble with acid.

4. Why does soda water effervesce when taken from the tank ?

5. Explain how a fire extinguisher puts out a small fire.

6. Why is rain-water preferred for washing purposes in limestone regions ?

7. It has been calculated that an average man exhales 464.5 liters (standard conditions) of carbon dioxide in a day. Calculate how many grams of starch a plant could make from this.

8. How could you prove that there is carbon in alcohol ?

9. How could you distinguish carbon dioxide from the monoxide.

10. Explain why cases of asphyxiation occur after coal stoves have been filled and left for the night.

11. Calculate the weight of steam that could be decomposed by a ton of incandescent coke containing 90 % carbon.

12. Write the equation for the reaction you would expect if carbon monoxide was passed over hot copper oxide.

13. How would you determine whether a gas was hydrogen or carbon monoxide ?

14. Why is it that such a large percentage of the cases of asphyxiation from water gas result fatally ?

CHAPTER XXV.

SILICON AND BORON.

242. Silicon. — Silicon, next to oxygen, is the most abundant element in the earth's crust. Nearly all the common rocks are silicon compounds. Silicon, as an element, is of little practical importance. Like carbon, it exists in three allotropic forms: a brown amorphous powder; a dull gray crystalline form, like graphite; and in octahedral crystals.

243. Varieties of Silicon Dioxide. — Silicon dioxide, or *silica*, SiO_2 , is the most common compound of silicon. It is found in many varieties, which differ in color and structure owing to minute quantities of impurities, and to conditions under which it is formed. Quartz, the most common form, crystallizes in hexagonal prisms, surmounted by a pyramid (Figs. 22 and 84). Clear crystalline varieties are known as rock crystal; purple varieties as amethyst. Rose quartz, milky quartz, and smoky quartz, or cairngorm stone, are other colored varieties of silicon dioxide, which, indeed, is found in all shades and tints. Chalcedony is cryptocrystalline and waxlike. Onyx and agate are varieties of chalcedony. Jasper and flint are other forms of silica. Opal is a hydrated form.

The shells of diatoms and many other microscopic organisms are siliceous, and deposits of these comprise the infusorial or diatomaceous earth. Sand is water-worn silicon dioxide, and sandstone consists of particles of sand cemented together.

244. Properties and Uses of Silicon Dioxide.—Silica is harder than glass; it is insoluble in ordinary reagents, but will dissolve in melted alkalis. Melted in the oxy-hydrogen flame, quartz can be drawn into delicate elastic threads, which are used in scientific instruments.



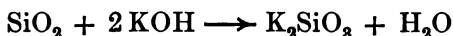
Fig. 84. Mass of quartz crystals.

White sand, which is nearly pure silica, is used in making glass and porcelain. Common sand is discolored by impurities, and if the particles are sufficiently irregular and angular it can be used in sandpaper and mortar. Sandstone is used for building; hard varieties are used for grindstones and millstones. Ground glass is glass roughened by blowing sand against it by means of a blast of air. Many clear varieties of quartz are cut and polished for jewelry, as amethyst, agate, carnelian, false topaz, and imitation diamond. The clear rock crystal is cut for lenses. Petrified wood has been formed by the gradual

replacement of the woody fibre by silica, preserving the woody structure. Cut and polished petrified wood is used as an ornamental stone. The fine varieties of infusorial earth are used as abrasives in polishing-powders, and are also used in cements, in refractory fire-brick, and as an absorbent in dynamite.

Silica is found in the ashes of most plants, especially in the ashes of stalks and stems. It imparts firmness to the stems and to the resistant exterior coating of straws and bamboo. The quills of feathers, claws, and nails contain considerable silica.

245. Silicates. — Silicon dioxide, like carbon dioxide, reacts with alkalis to form salts called silicates:



Sodium and potassium silicates are soluble in water; nearly all the other silicates are insoluble, stable compounds, which comprise the larger part of the earth. Such minerals as felspar, mica, hornblende, clay, and talc are silicates, various mixtures of which comprise the common rocks, as granite, gneiss, and slate.

Sodium and potassium silicates are made by melting the metallic hydroxides, or carbonates, with silicon dioxide. The thick water solution is used in filling soaps, in making artificial stone and cement, in wall coloring, calico printing, and fireproofing wood and textiles.

246. Glass. — Glass is a *mixture of silicates*. Common, crown, or window-glass, consists of silicates of sodium and calcium; Bohemian glass, of potassium and calcium silicates; flint glass contains silicates of lead and potassium.

Glass is made by melting together sand, an alkali, and

calcium carbonate in pots of fire-clay (Fig. 85). The alkali may be sodium or potassium carbonate or a mixture of these. An oxidizing agent, as potassium nitrate or manganese dioxide, may be added to remove the green

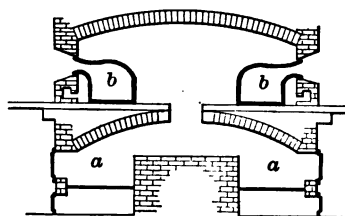


Fig. 85. Glass furnace:
a, fire-boxes; b, melting-pots.

color due to iron compounds. The mixture is heated to a high temperature and thoroughly melted, the gases given off aid the mixing, and any infusible impurities coming to the top are skimmed off. When the mass is cooled to a pasty condition, it may be blown or moulded.

Window-glass is made by the workman taking a mass of the molten glass on the end of a long iron blowpipe, and blowing it into a large bubble. This is drawn out into a cylinder by swinging it and rolling it on a plate. The ends of the cylinder are cut off, a cut is made lengthwise, and the glass is spread out flat. *Plate glass* is made by pouring the molten glass on a bronze table, rolling it with a hot iron cylinder (Fig. 86), and finally polishing it. *Cut glass* is flint glass moulded to the desired shape; the design is cut by a wheel, and the glass polished with rouge or putty powder.

Cheap glass dishes and similar objects are made by pressing the plastic glass in a die. Bottles are blown in a mould. If the glass is cooled rapidly, it is hard, brittle, and liable to break under a shock; to overcome this it is annealed. The glass is passed slowly through a long furnace from the hot to the cooler end, so that the temperature is very gradually lowered.

Crown glass is a colorless window-glass used for convex lenses. *Bohemian glass* is harder and less fusible, and is used for chemical apparatus. *Flint glass* is brilliant, heavy, and soft, and is used for concave lenses, lamp chimneys, and globes, and for imitation gems, as paste diamonds.

Glass is colored by dissolving various substances in the melted mass. The green color of common glass is due to



By courtesy of *The Scientific American*.

Fig. 86. Rolling out plate-glass.

iron compounds in the sand and limestone; chromium compounds give a rich green. Compounds of copper and cobalt give blue color; manganese, pink to violet; manganese with iron, yellow to brown; silver, yellow; gold, ruby red; calcium fluoride, white and translucent.

All the silicon compounds mentioned contain oxygen, and while silicon forms many other and more simple compounds, few are of practical importance.

247. Silicon Carbide, or Carborundum. — Silicon carbide, carborundum, is a crystallized solid varying in color, and often brilliant and iridescent. It is extremely hard, and

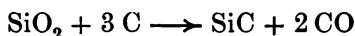


Fig. 87. Carborundum products.

is used as a substitute for emery for grinding and polishing in wheels, hones, and carborundum cloth (Fig. 87).

Carborundum is made in an oblong electric furnace, at the ends of which are metal plates to which are attached

the heavy carbon electrodes projecting into the furnace. The electric connection between the electrodes is through a mass of granulated coke. Sand is mixed with coke, a little salt, and sawdust. The salt is used to aid fusion, and the sawdust to make the mass porous. This mixture is piled around the central core of coke and held in place by side walls of loosely piled bricks (Fig. 88). The action in the furnace is not electrolytic, but is due to the heat generated through the resistance of the coke to the current. The carbon reacts with the melted sand to form carbon monoxide and carborundum:



The action continues for about eight hours. When the furnace has cooled, the sides are torn down and the carborundum removed (Fig. 89). The best crystals are found around the central core. The crystals are crushed,

washed with sulphuric acid, dried, and graded according to size.

Silicon hydride, SiH_4 , is made by blowing coal-gas through an electric furnace charged with silica. The hydride is a strong reducing agent, and burns, forming water and silicon dioxide.

Silicon fluoride, SiF_4 , is a colorless gas formed in the reaction of hydrofluoric acid, HF , with silica, SiO_2 , or glass. It decomposes in water, forming hydrofluosilicic acid, H_2SiF_6 , and silicic acid, H_2SiO_3 .

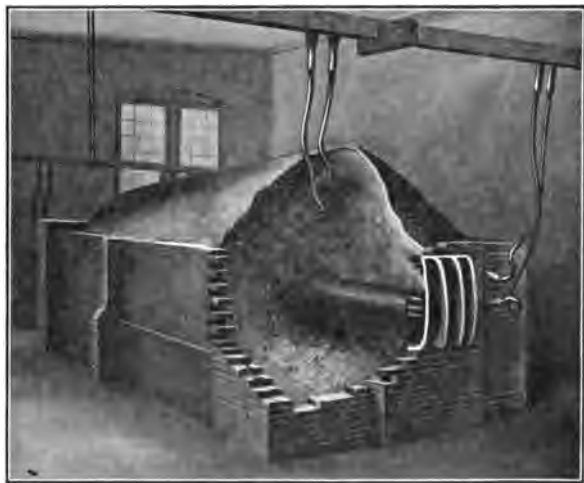


Fig. 88. Carborundum furnace, showing charge.

248. Boron and Boric Acid.—The element boron is of little importance. It is a brown powder, soluble in melted aluminum, and infusible at the temperature of the electric arc. Its important compounds are boric acid and borax.

Boric acid, H_3BO_3 , occurs in minute quantities in vapors arising from the earth in the volcanic regions of Tuscany,

in Italy. Although the amount of boric acid contained in the steam is small, it is retained by constructing shallow reservoirs surrounding the vents from which the steam escapes. The steam condensed in these reservoirs contains a considerable amount of boric acid. The reservoirs are arranged one below another on the hillside. After the steam has been allowed to condense in each for twenty-four hours, the solution is run into the one below and the process repeated. After the boric acid solution has become concentrated, it is evaporated in shallow pans, heated by

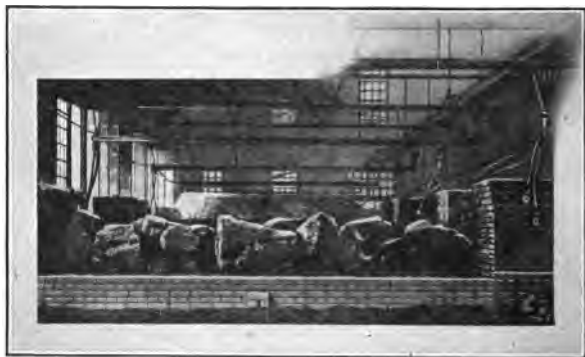


Fig. 89. Carborundum furnace after burning (sides removed).

steam from other jets. The boric acid separates and is purified by recrystallization. Most of the boric acid used in the United States is made by the reaction of borax with an acid.

Boric acid is obtained in fine crystalline scales. It is a weak acid, sparingly soluble in water. It is used as an antiseptic and as a preservative.

249. Borax. — When boric acid is heated, it loses water, forming successively metaboric acid, $H_2B_2O_4$, and pyroboric

acid, $\text{H}_2\text{B}_4\text{O}_7$. Sodium pyroborate, $\text{Na}_2\text{B}_4\text{O}_7$, is the familiar compound, borax. There are large deposits of borax and calcium borate in California, which supply this country. Borax is also obtained from the boric acid of Tuscany.

Borax is obtained from solutions in large crystals, containing either 5 or 10 molecules of water of crystallization, according to the temperature at which they are deposited. Ordinary borax has the composition $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. When heated, crystallized borax swells during the evaporation of the water of crystallization and then melts to a clear glassy mass. Fused borax dissolves metallic oxides, and these often impart to the glassy mass a color characteristic of the metal. Thus, cobalt compounds give a blue color, and manganese compounds a violet color, to a drop of fused borax heated in the oxidizing flame. A solution of borax has a feeble alkaline reaction.

**Borax
bead tests.**

Borax is used in soldering and welding to dissolve the metallic oxides formed. It is employed in large quantities as an antiseptic and preservative.

Summary.

Silicon is a very abundant element of little practical importance.

Its most common compound is *silicon dioxide*, occurring as quartz and sand and as a constituent of many rocks.

Silica is very hard and fuses only at high temperatures. It is used in making glass, mortar, and polishing-powders.

Sodium and potassium *silicates* are soluble.

Glass is a mixture of silicates. Three varieties are crown, flint, and Bohemian glass. The materials are melted together and blown or moulded into shape while plastic. Colors may be added to it while in a melted state.

Silicon carbide is made by heating coke and sand in an electric furnace. It is used as an abrasive.

Silicon fluoride is produced by the action of hydrofluoric acid on glass.

Boric acid is found in nature, but much of it is made from borax.

Borax occurs in large deposits in California.

It gives characteristic reactions with metallic oxides used as bead tests.

Borax is used in soldering and welding, and as a preservative.

Exercises.

1. Why is not silicon found uncombined in nature?
2. Give the most important uses of silicon dioxide.
3. Give the composition and uses of the chief varieties of glass.
4. Why is sand the main final product of long-continued disintegration of rock materials by water?
5. What is water-glass? How is it made, and what are its uses?
6. Describe the manufacture of carborundum, and give its uses.
7. Calculate the percentage of water of crystallization in borax.

CHAPTER XXVI.

CALCIUM AND ITS COMPOUNDS.

CALCIUM.

250. — Although metallic calcium has been known for many years, it is only recently that it has been made in any quantity. Sir Humphry Davy was the first one to see the metal, but failed to get enough to determine its properties. The credit for the successful isolation of the metal belongs to Dr. Robert Hare, a scientist of Philadelphia. His electrolytic method, with some modifications, is the one now used to obtain the metal.

251. Preparation. — Metallic calcium is prepared by passing an electric current through fused calcium chloride contained in a crucible of graphite, which acts as the anode (Fig. 90). At first the cathode is an iron rod (*B*), capable of being raised by a screw mechanism (*A*). The calcium deposits on the end of the iron rod, solidifies, and grows downward as an irregular cylinder. This rod of calcium becomes the cathode (*C*) as the iron rod is gradually raised out of the molten chloride by the screw mechanism. A coating of calcium chloride protects the calcium from oxidation as it emerges from the molten bath. By using suitable screw mechanism, pieces of calcium several feet long can be obtained. The electric current, by its passage, keeps the calcium chloride molten in the graphite crucible, except at the bottom (*D*), where it

is kept cold, and solidified by water running through a copper coil (*EE*). Most of the chloride adhering to the sticks of calcium is removed by hammering; the remainder is dissolved off by alcohol.

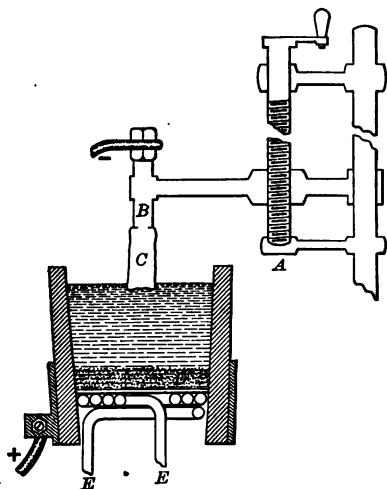


Fig. 90.

252. Physical Properties.—Pure calcium is a silver-white metal of brilliant lustre, and is a little lighter than magnesium. It is harder than lead or tin, almost as hard as aluminum, but softer than zinc. At 300° to 400° C. it is as soft as lead and can easily be rolled or hammered. Only four

metals surpass calcium as conductors of electricity.

253. Chemical Properties.—Calcium is a much less active metal than has been imagined. It keeps its lustre in dry air and can be preserved without difficulty in a stoppered bottle. In moist air its surface becomes dulled. The solid metal does not ignite when heated red-hot, but when sent whizzing through the air against a brick wall bursts into a brilliant white flame and burns violently, like magnesium. Molten calcium burns vigorously in oxygen and in chlorine.

Water is *slowly* decomposed by calcium, and hydrogen is evolved at a rate very convenient for the collection

of the gas. As a reducing agent in the manufacture of certain drugs and dyes, calcium is superior to sodium because it is more moderate in its action and less dangerous to use.

254. Uses.—An authority on electrolytic processes states that calcium could be prepared on a large scale for less than ten cents a pound. At such a price it would no doubt become available in important technical processes. Calcium may form valuable alloys owing to its lightness, strength, or electric conductivity. It has been recommended for the dephosphorization of steel.

CALCIUM CARBONATE.

255. Occurrence.—Calcium carbonate, CaCO_3 , is one of the most abundant compounds occurring in nature. In the form of limestone it constitutes whole mountain ranges. Marble, which exists in enormous quantities in various parts of the world, is a purer form of calcium carbonate than limestone. Marble was formed from limestone by the action of heat and pressure under such conditions that carbon dioxide, which generally is given off when limestone is heated, was prevented from making its escape. The mineral matter in shells is chiefly calcium carbonate derived from the water in which the animals lived. In past ages, deposits of shells became cemented together into rock materials. Coquina, or the loose shell rock of Flor-



Fig. 91. Coquina.

ida, illustrates an early stage of this process (Fig. 91), and limestone a more complete transformation.

Calcite is a pure crystalline form of calcium carbonate, and one of its varieties, Iceland spar, gives a double refraction of light (Fig. 92). In many other minerals, such as chalk and dolomite, calcium carbonate is present.

256. Properties. — When pure, calcium carbonate is a white solid, often transparent. The color of limestone and many varieties of marble is due to the presence of impurities. Calcium carbonate occurs naturally in amorphous masses and in crystals of different forms. When precipitated from solutions of calcium salts by soluble carbonates, it comes down at first as amorphous scales and later as minute



Fig. 92. Iceland spar.

crystals. It is only very slightly soluble in pure water, but, as we have already seen (§ 236, 237), it is more soluble in water containing dissolved carbon dioxide. The hardness of water in limestone regions causes it to form a closely adhering deposit on all vessels in which it is boiled, since boiling decomposes the calcium bicarbonate, driving off part of its carbon dioxide and leaving the insoluble carbonate. This deposit, known as *boiler scale*, clogs the tubes of steam boilers. Hence the water is usually softened before being introduced into the boilers.

The formation of underground caverns in limestone regions is due to the production, solution, and decomposition of the bicarbonate. Charged with carbon dioxide from decaying organic materials, the soil water dissolves

limestone and sinks through cracks in the rocks, widening them as it goes. Reaching a less soluble stratum of rock, it flows along this, but dissolves the limestone above. This action, continuing for centuries, finally excavates a cave, such as Mammoth Cave in Kentucky and Luray Cavern in Virginia. As soon as these caves are hollowed out, a new process sets in. The water,



Fig. 93. Stalactites and stalagmites in a limestone cave.

before it drops from the roof, loses some of its carbon dioxide, and part of the bicarbonate is converted into the insoluble carbonate. This is left behind on the roof of the cave. The drops that fall to the floor lose more carbon dioxide and some water by evaporation, and likewise deposit calcium carbonate. The final result of the process is the formation of hanging masses of calcium carbonate,

like icicles of stone, known as *stalactites*, and the formation of pointed mounds below called *stalagmites* (Fig. 93). In this way the cave may become nearly filled again.

257. Uses. — Natural calcium carbonate has three very important uses. Large quantities of limestone and marble are used as building stone. Enormous amounts of limestone are yearly *burned* (heated to expel the carbon dioxide) to form quicklime. It will be remembered that the lime unites with sand when strongly heated to form calcium silicate, a compound which is fusible at high temperatures. The third use of limestone depends upon this property. When iron ore contains silica, limestone is mixed with the ore to act as a flux; that is, to make the fusion more easy. When this mixture is heated with coke in a blast-furnace, the silica unites with the lime to form the slag, and the iron is obtained free.

CALCIUM OXIDE.

258. Manufacture of Lime. — Calcium oxide, or *quicklime*, is made by the decomposition of calcium carbonate at a red heat:



The furnace or kiln (Figs. 94, 95) in which the calcining occurs is essentially a long shaft with a fire (*a*) near the bottom, so arranged that only the flames and hot gases of combustion come in contact with the charge of limestone, marble, or shell in the shaft. The quicklime formed is withdrawn from time to time at the bottom (*b*) of the shaft, thus causing a slow sinking of the charge. By withdrawing the slide (*c*) the lime tumbles into a chamber below.

Many kilns in this country are made of brick or large blocks of limestone. Several feet from the bottom of the shaft a limestone arch walls off a fire-box. Numerous small holes are left in the limestone arch to allow the flames and hot gases from the burning fuel to enter the portion of the shaft above. The lime made by this *long-flame process* is not made impure by the ash from the fuel. If the limestone contains impurities, as silica, iron, or aluminum, in any considerable amount, a poor quality of lime is obtained. The successful operation of the kiln depends largely upon the efficient removal of the waste gases from the shaft so that the decomposition of the carbonate is not checked.

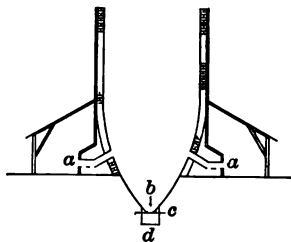


Fig. 94. Lime-kiln (section).

259. Properties and Uses. — Pure calcium oxide is a soft,

white, non-crystalline powder which can only be fused and vaporized at the temperature of the electric arc (3000°).

It slowly takes up moisture, forming the hydroxide:

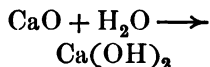


Fig. 95. Lime-kiln at Yellow Springs, Ohio.

When water is put on lumps of quicklime, cracks soon appear on the surface, the mass swells, and finally falls to

a voluminous white powder. The heat of combination is so great that the lime becomes hot, and clouds of steam arise. This energetic action or process is called *slaking*,

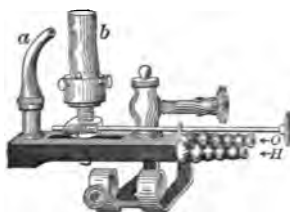


Fig. 96. Lime-light burner.

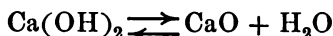
and the product of the reaction, calcium hydroxide, is called *slaked lime*. When quicklime is left exposed to the air, both water and carbon dioxide are taken up, with the formation of calcium hydroxide and calcium carbonate. This process is known as *air-slaking*.

On account of its infusibility and dazzling incandescence in the oxy-hydrogen flame, the oxide is used in the calcium or lime-light. A lime-light burner is shown in Fig. 96; *a* is the burner tip for an oxy-hydrogen flame, and *b* is the cylinder of quicklime. Many other uses of calcium oxide are considered in connection with the hydroxide.

CALCIUM HYDROXIDE.

260. Properties and Uses. — Calcium hydroxide, or slaked lime, is a soft white solid when pure, and is sparingly soluble in water, forming a solution called *lime water*. Lime water, white with suspended but undissolved particles of the hydroxide, is known as *milk of lime*.

When heated, the hydroxide loses water and is reconverted into the oxide, showing the reaction to be a reversible one, according to the temperature:

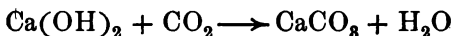


The water solution of calcium hydroxide is strongly basic, which property has led to its wide use as a cheap alkali.

In this respect it stands among the bases as sulphuric acid does among the acids.

Lime, as a cheap base, is used in the manufacture of alkalies and bleaching-powder, in glass-making, in the removal of hair from hides, and in many other industries. The chief use, however, is in the preparation of mortar and cement.

261. Mortar and Cement. — Mortar is a slaked lime mixed with water and three or four times its bulk of sand. The hardening is due to the drying out of the water and the slow absorption of carbon dioxide from the air:



The formation of the calcium carbonate occurs first in the outer layer of the mortar, and years may be required to affect the inner layers. The sand makes the mortar porous, so carbon dioxide can gain access to form the carbonate, and also prevents shrinkage and cracking as the mortar dries. Moreover, the minute crystals of calcium carbonate formed become entangled with the sharp points of the grains of sand, making a rigid, coherent mass.

Many cements are made by strongly heating mixtures of limestone and clay and then grinding the product. The burning forms complex compounds which have the power of taking on water of crystallization, and setting to a hard, rigid mass. The hardening of cement can take place under the water, and the transformation occurs throughout the whole mass within a short time. The hardening of mortar, however, depends upon the access and absorption of carbon dioxide, and does not begin until most of the water has evaporated. Then the action proceeds very slowly inward.

CALCIUM SULPHATE.

262. Varieties. — Calcium sulphate is, after the carbonate, the most abundant and widely distributed salt of calcium. It occurs as the mineral anhydrite, CaSO_4 , and as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Satinspar, alabaster, and selenite are varieties of gypsum. Selenite is often found in large, transparent crystals that can be scratched with the finger nail.

263. Properties and Uses. — Gypsum is but sparingly soluble in water; its solubility increases to 40° and then decreases. When heated, gypsum loses three-quarters of its water of crystallization, and the residue may be said to have one molecule of water of crystallization to every two molecules of calcium sulphate $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. The chalky powder resulting from the heating is known as *plaster of Paris*. On a large scale it is made by heating in kilns a charge of gypsum broken into small lumps to insure evenness in "burning." Care is taken not to overheat; 125°C . is the most favorable temperature for the process.

When plaster of Paris is wet, water is again taken up, forming needles of crystallized gypsum which, becoming entangled, set or harden the mass. The hardening is also accompanied by a slight increase in volume. This property explains the use of plaster of Paris in making casts. The slight expansion secures a sharp impression of the mould. The powder is mixed with about a third its weight of water, the pasty mass put into the mould, and in less than half an hour the plaster sets. The ivory surface of casts is secured by dipping them in melted paraffin or by painting them with a solution of paraffin in

petroleum ether. The solvent in the latter case evaporates, leaving the waxy filling in the pores of the cast and making it impervious to water. Many beautiful metallic objects are now made by plating a thin film of metal on a plaster of Paris base. Plaster of Paris is also used for rigid bandages in surgery and as a surface coating for walls. *Stucco* is plaster of Paris and rubble, mixed with sizing or glue instead of water.

264. Calcium Phosphates.—The phosphates of calcium are of great importance to organic life. The bones of animals are essentially *normal calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$. This compound occurs as phosphorite which has been derived from animal remains. *Guano* contains phosphorite in addition to nitrogenous compounds. Phosphates are an important plant food, but to be available must be in a soluble form that can be taken up by the plants. The soluble phosphates result from the decomposition of rocks containing phosphates. Since the process is a slow one, the supply of phosphates in cultivated soils often becomes exhausted. To supply this need, the manufacture of soluble phosphates for fertilizers has grown to be an important industry.

The *superphosphate of lime*, $\text{CaH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, is the most important artificial fertilizer. It is made by treating phosphorite or bone-ash with crude sulphuric acid. The superphosphate formed is readily soluble in water, and when spread upon the soil is available for plant use.

265. Bleaching-Powder.—Bleaching-powder, or chloride of lime, is made by passing chlorine over freshly slaked lime spread on the floors of a series of absorption chambers (Fig. 97). Chemists are still in doubt as to the

reactions involved in the process and the formula of the product. The latter, however, is often represented as CaOCl_2 .

Bleaching-powder is an unstable white powder which is slightly soluble in water. When bleaching-powder is treated with acids, chlorine is evolved. Hence the powder is used as a source of chlorine for bleaching purposes.



Fig. 97.

The cotton or linen to be bleached is freed from grease and oil. The cloth is next soaked in a solution of bleaching-powder, then dipped in dilute acid, and finally thoroughly washed to remove the chemicals (cf. § 57). The solutions used are very weak, to prevent injury to the fibre of the cloth.

When exposed to the air, bleaching-powder slowly decomposes, with the absorption of carbon dioxide. As a result chlorine is liberated, and for this reason the powder, often called "chloride of lime," is used as a disinfectant and germicide.

Summary.

Calcium, although very abundant in nature, is rarely seen as metal.

It can be obtained by the electrolysis of fused calcium chloride.

The most important *calcium compounds* are:

- the carbonate (limestone, chalk, marble);
- the hydroxide (slaked lime);
- the oxide (quicklime);
- the phosphate (phosphorite);
- the sulphate (gypsum).

Lime is made by heating calcium carbonate. Slaked lime is made by adding water to quicklime.

Slaked lime is used in making mortar, which hardens by the evaporation of water and the absorption of carbon dioxide.

Plaster of Paris is made by partly dehydrating gypsum. It is used in making plaster casts.

Calcium phosphates, derived from bone-ash and mineral beds, are used in making fertilizers.

Bleaching-powder is made by passing chlorine over slaked lime. It is used in bleaching and as a disinfectant.

Exercises.

1. Why is the production of lime hastened by blowing air or steam into a lime-kiln?

2. How could quicklime be made from slaked lime?

3. In the laboratory, loosely stoppered bottles that contain quicklime are sometimes found with the sides broken out. How would you account for this?

4. Lime-water standing exposed to air becomes coated with a film of insoluble substance. What is the substance? Explain its formation.

5. Compare the hardening of mortar with that of plaster of Paris.

6. For what reason is normal calcium phosphate converted into "superphosphate" in the manufacture of fertilizers?

7. Calculate the weight of quicklime which a manufacturer might expect to get from 1000 kilograms of pure limestone. What weight of carbon dioxide would be given off during the action? What volume would the gas have, standard conditions?

8. What weight of nitric acid would be required to neutralize 35 grams of calcium hydroxide?

9. What weight of water enters into combination in slaking 500 lb. of quicklime?

10. Compare the electrolytic processes for making sodium and calcium.

CHAPTER XXVII.

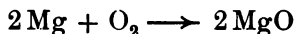
MAGNESIUM, ZINC, AND MERCURY.

MAGNESIUM.

266. Occurrence and Preparation. — Although magnesium is of comparatively little importance in a commercial way, its compounds are very abundant in nature. The most important of these are dolomite, a double carbonate of calcium and magnesium; magnesite, a carbonate; various silicates, of which asbestos and hornblende are examples; carnallite, a double chloride of potassium and magnesium, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. Magnesium sulphate is found in certain mineral waters.

The metal is commercially obtained by the electrolysis of carnallite. The salt is fused, together with some common salt or cryolite, in an iron crucible which serves as the cathode. A carbon rod serves as the anode.

267. Properties and Uses. — Magnesium is a silvery white metal of low specific gravity. It resembles both calcium and zinc in its properties, and stands between them in metallic character. It decomposes water slowly at 100° , but does not affect it at ordinary temperatures. Moist air acts on magnesium slowly. It burns with comparative ease, with the evolution of a brilliant white light of great actinic power. The oxide is formed in this reaction :



Dilute acids react with magnesium very readily, hydrogen usually being evolved.

The common salts of magnesium are stable substances, soluble in water, with the exception of the carbonate and the phosphate.

Magnesium is used in flashlight preparations for photographic purposes because of the actinic power of the light it gives in burning. It is also used in making fireworks.

268. Compounds of Magnesium. — The formulas of the magnesium compounds show that the element has a valence of two, or we may say it forms bivalent ions.

Many magnesium compounds, when heated in an oxidizing flame, are converted into magnesium oxide. This, when moistened with a solution of cobalt nitrate and heated, yields a mass having a pale pink color.

Magnesium is one of the few elements that enter into direct combination with nitrogen. When nitrogen is passed over red-hot magnesium, magnesium nitride, Mg_3N_2 , is formed.

Mixtures of magnesium carbonate with magnesium hydroxide are used in pharmaceutical preparations and in face powders.

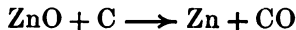
Several salts of magnesium are used medicinally. One of these, the sulphate, is found in nature as *Epsom salts* ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Certain spring waters owe their laxative properties to the presence of magnesium salts.

ZINC.

269. Extraction from Ores. — Zinc is not found in the uncombined state. Its common ores are zinc-blende, ZnS ; smithsonite, ZnCO_3 ; zincite, ZnO .

To separate zinc from the oxide, the ore is finely powdered and mixed with coal. The mixture is then heated

in earthenware retorts (Fig. 98, *a*). The carbon reduces the zinc oxide :



The temperature in the process is raised above the boiling-point of the metal, 950° , which consequently passes off as gas, and is condensed in earthenware or iron receivers (*b*).

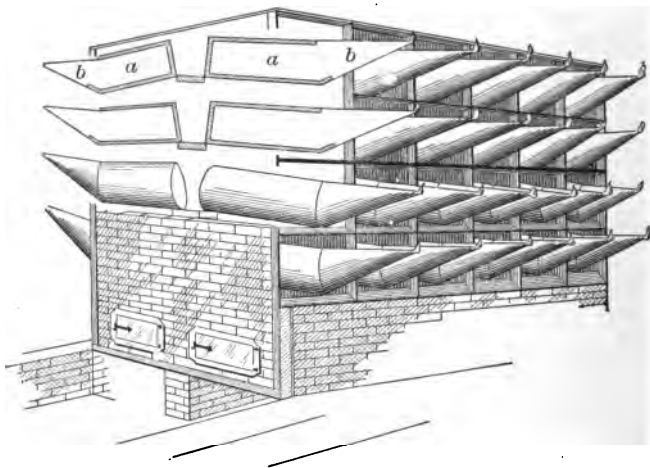
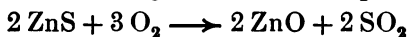
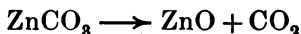


Fig. 98.

When the ore is not an oxide, a preliminary operation must precede the reduction. This consists in heating the ore on grates in contact with air. The operation is known as *roasting*, and converts the metal into an oxide. In the case of zinc sulphide, care is taken not to convert it into the sulphate.



The oxide that results in these reactions is then reduced

with the carbon in the manner that has been described. The silicate is reduced directly. A rotary roasting-furnace is shown in Fig. 99. The ore is dumped through the hopper (*b*), and the flames from the fire-box (*a*) sweep over the ore as the hearth slowly rotates; *c, c* are the fume chambers.

Zinc, as extracted from its ores, usually contains carbon, arsenic, cadmium, and other impurities. It is freed from these by distillation.

270. Physical Properties. — Zinc is bluish white in color. It comes into the market in the form of heavy bars called *ingots* or *spelter*, formed by pouring the melted metal into moulds. In this form the metal is crystalline in structure and rather brittle. Between 100° and 150° it is malleable and ductile, and can be rolled into sheets. After having been obtained in this form, it remains malleable at ordinary temperatures. At 300° it again becomes brittle and can be powdered.

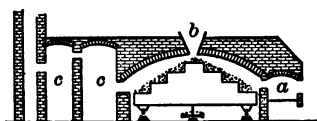
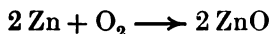


Fig. 99.

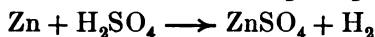
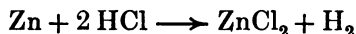
Granulated or *mossy* zinc is a form much used in the laboratory. It is made by pouring the melted metal into water. *Zinc dust* is obtained in the distillation of the metal. As long as the receiver remains comparatively cold, the distilled zinc collects in the form of a powder. This operation is similar to the one by which sulphur is obtained as flowers of sulphur. Zinc dust always contains a certain amount of the oxide.

271. Chemical Properties. — Zinc is regarded as distinctly metallic, but it differs considerably from such

metals as calcium and sodium. It resembles cadmium and magnesium more closely. Zinc does not act on water at ordinary temperatures. Air attacks it slowly in the presence of moisture, forming a basic carbonate, which acts as a protective coating, so that only the outer layer of the metal is affected. When zinc is heated in air or oxygen, it burns with a bluish flame, forming zinc oxide.



Zinc reacts readily with dilute acids, forming zinc salts, and, as a rule, liberates hydrogen :



In acting on zinc (or other metals) nitric and sulphuric acids, if concentrated, do not liberate hydrogen, since they act as oxidizing agents and convert the hydrogen into water. In these cases, the gases that are given off are reduction products of the acids. In the case of sulphuric acid, sulphur dioxide is obtained (§ 146); from nitric acid, nitric oxide or nitrogen peroxide is produced (§ 173).

The action of dilute acids on zinc is hastened by the presence of certain solid substances in contact with the metal. Pure zinc will scarcely react with acids, but if it is impure, solution takes place with great rapidity. A similar effect is produced by the presence of a very small amount of copper, or other metal, as a deposit on the surface of the zinc. In these cases the particles of carbon or copper act like cathode plates of a voltaic cell. Hence the velocity of the evolution of hydrogen from acids is increased by their presence.

Many compounds of zinc, when heated on charcoal or on a plaster block before a blowpipe, yield zinc oxide, yellow

when hot, and white when cold. If the oxide is moistened with a drop of a solution of cobalt nitrate, and again heated, a bright green mass containing a compound of zinc and cobalt oxide is obtained. Figure 100 shows the plaster of Paris blocks with a hollow, made by the forceps, to contain the compound to be tested by heating with cobalt nitrate.

272. Uses.—Zinc is used in making several important alloys. *Brass* is composed of copper and zinc; *German silver* contains zinc, copper, and nickel; *bronze* sometimes contains zinc in addition to copper and tin.

Galvanized iron is iron covered with a thin layer of zinc, which acts as a protective coating and prevents rusting. The iron is first cleaned and then dipped into molten zinc. Of late an electrolytic method of galvanizing has come into use. The process is analogous to copper or silver plating. Another important use of zinc is for the anode plates of batteries.

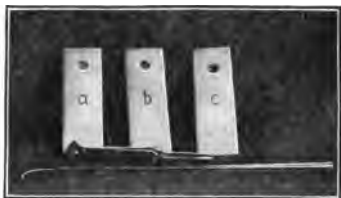
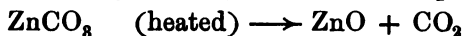
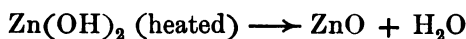
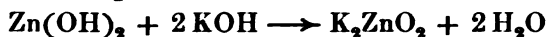
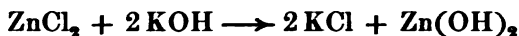


Fig. 100.

273. Zinc Oxide and Hydroxide.—Zinc oxide, ZnO , is much used as a base for white paints. It does not have as great covering power as white lead, but it has the advantage of not turning black from contact with hydrogen sulphide. It can be made by burning zinc or by heating zinc hydroxide or zinc carbonate:



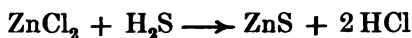
On adding potassium hydroxide to a solution of a zinc salt, zinc hydroxide is precipitated, since this substance is insoluble in water. If an excess of potassium hydroxide is added, the hydroxide is dissolved, forming potassium zincate.



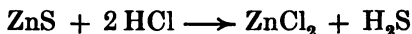
274. Salts of Zinc.—*Zinc chloride*, ZnCl_2 , is obtained by the action of hydrochloric acid and zinc. It is an extremely deliquescent substance, sometimes used as a drying agent. It also has the power to dissolve metallic oxides; because of this property it makes a good flux for soldering metals. Wood which has been soaked in a solution of zinc chloride resists decay.

Zinc sulphate, ZnSO_4 , is used in making battery solutions.

Zinc sulphide, ZnS , found in nature as zinc-blende, can be precipitated from solutions of zinc salts by the addition of hydrogen sulphide:



But this reaction is reversible; that is, zinc sulphide will dissolve in dilute hydrochloric acid with the formation of zinc chloride and hydrogen sulphide:



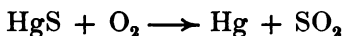
For this reason, the reaction shown in the first equation is never complete; for when a certain amount of hydrochloric acid has been formed, the second reaction begins to take place. Hydrogen sulphide is only slightly ionized but its ions are necessary for the first reaction. If, however, an acid is present, its hydrogen ions force back the dissociation of hydrogen sulphide to such an extent that the number of sulphur ions present is very small. If we dis-

pose of the hydrogen ions as fast as they are formed, by adding such a substance as ammonium hydroxide, the precipitation of the zinc sulphide will be complete. If, on the other hand, much acid is present in the solution, the precipitation will be entirely prevented.

All soluble zinc salts are poisonous.

MERCURY.

275. Occurrence and Separation.—Mercury is found only in a few localities, the deposits of Spain and California being the most important. It occurs native in small drops mixed with earthy materials, and in the sulphide, *cinnabar*, HgS. From the latter it is obtained by roasting, so as to convert the sulphur into the dioxide and vaporize the mercury, which is condensed and purified:



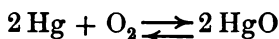
276. Physical Properties.—At ordinary temperatures, mercury, commonly known as *quicksilver*, is a silvery-white liquid, with a brilliant metallic lustre. Its density is greater than that of lead, so that iron easily floats on it. Mercury solidifies to a substance resembling tin at about -40° , and boils at a temperature below red heat, but vaporizes slowly at ordinary temperatures. It is a good conductor of electricity. The molecular weight of mercury, as found from its vapor density, is the same as the atomic weight, 200; hence there is one atom in the molecule of mercury vapor.

Mercury has the power of dissolving many other metals, forming alloys with them called *amalgams*. Mercury dropped on a gold ring will whiten it by amalgamating with the gold. These amalgams are **Amalgams.** not true compounds, as they may be formed in varying

proportions. When there is a large excess of mercury, amalgams are liquid; otherwise they are solid.

The vapor of mercury is highly poisonous, as is the metal itself when finely divided. Mercury can be obtained as a fine gray powder by shaking it violently with flour, grease, or any substance which will coat the minute drops and prevent them from uniting to form a fluid mass. This process, known as *extinguishing*, is used in the preparation of blue pills and mercurial ointments.

277. Chemical Properties.—Mercury combines readily with the halogens and sulphur. Oxygen does not combine with it at ordinary temperatures, but at high temperatures it forms oxides, which at still higher temperatures dissociate into mercury and oxygen. This is shown by the reversible equation:

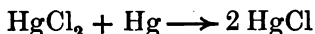


Pure dilute acids do not attack mercury. Concentrated nitric acid dissolves it readily, and dilute nitric acid also attacks it in the presence of nitrogen peroxide.

278. Uses.—Mercury is used in important scientific instruments, such as the thermometer, barometer, and others. It is also used for the collection of gases soluble in water. Its most important uses, however, are in the various amalgams. Sodium amalgam finds considerable use in the laboratory, and tin amalgam is used to coat the back of mirrors. Amalgams of silver and other metals are used in filling teeth. Gold and silver are extracted by allowing the crushed ore to flow in a thin mud over tables covered with mercury. The gold amalgamates with the mercury, from which it can be separated by distilling the mercury.

279. Compounds of Mercury. — Mercury forms two series of compounds, the mercurous and the mercuric. The chlorides are the most important salts, and may be taken as typical of the two series.

Mercurous chloride, known as *calomel*, has its composition represented by the formula HgCl . Since it is insoluble in water, it may be prepared by treating a solution of a mercurous compound with a chloride. It is produced commercially by heating a mixture of mercuric chloride and mercury, when it sublimes as a white powder: Calomel.



Exposed to the light, mercurous chloride slowly blackens on account of the liberation of mercury by the reversal of the above reaction. It is extensively used in medicine.

The common name of *mercuric chloride* is *corrosive sublimate*, and its formula is HgCl_2 . It is made by heating a mixture of sodium chloride and mercuric sulphate; the chloride sublimes, as its name indicates. Corrosive sublimate. The sublimate is a white, translucent mass, from which the salt can be obtained in silky needles by dissolving in water and recrystallizing. It is slightly soluble in water at ordinary temperatures, but at higher temperatures it is more soluble. Corrosive sublimate is a violent poison. It is also a powerful antiseptic and germicide. For this purpose, very dilute solutions are used (1 part to 1000 parts of water), as its antiseptic properties increase with the ionization. Hence the dilute solutions in which the salt is fully ionized are better antiseptics than the more concentrated ones. With the alkaline chlorides it forms double salts more soluble than mercuric chloride by itself, and much used in making antiseptic solutions.

MAGNESIUM.

Exercises.

1. How is magnesium prepared from carnallite?
2. For what is magnesium used?
3. Magnesium oxide is slightly soluble in water. Would the solution give an acid or an alkaline reaction? Why?
4. What reaction takes place when dilute sulphuric acid is added to magnesium?
5. What is Epsom salts?
6. Mention two ways by which carbon dioxide could be obtained from magnesite.
7. How many grams of magnesia, MgO , could be prepared by heating 20 lb. of magnesium carbonate?
8. When 0.362 gram of magnesium was added to an excess of dilute acid, 365 c.c. of hydrogen were liberated. At the time the measurement was made, the temperature was $21^{\circ}C$. and the pressure was 770 mm. From the data given, calculate the hydrogen equivalent of magnesium.
9. Using your answer to 8, calculate the atomic weight of magnesium.
10. What is a test for a magnesium compound?

ZINC.

Summary.

Zinc is usually obtained by roasting the ore and then reducing the oxide.

Spelter, sheet zinc, granulated or mossy zinc, and zinc dust are commercial forms of zinc.

Brass and German silver are common alloys of zinc.

Zinc is bivalent.

Zinc hydroxide acts as a base in the presence of strong acids and as an acid in the presence of strong bases.

The carbonate, chloride, sulphide, and sulphate are common compounds.

Exercises.

1. Starting with zinc carbonate, describe the preparation of four commercial forms of zinc.
2. Name two alloys of zinc and tell what each contains.
3. Why does zinc corrode very slowly in air?
4. Name a compound of zinc used as a paint base. Why is it of value in making paint for use in chemical laboratories?
5. Name a compound which would form zinc hydroxide on the addition of the right amount of hydrochloric acid.
6. Write equations showing how hydrogen could be produced by the reaction of either an acid or a base with zinc.
7. Why is wood sometimes impregnated with a solution of zinc chloride?
8. Why is tin-plate, preparatory to soldering, often wet with a solution of zinc chloride?
9. Why will not hydrogen sulphide completely precipitate zinc, as zinc sulphide, from a solution of zinc sulphate?
10. Explain the fact that water solutions of zinc sulphate give an acid reaction.
11. Describe a test for zinc.
12. How many grams of zinc would be required to replace the hydrogen contained in 15 grams of sulphuric acid?
13. Mention two ways by which zinc sulphide can be formed.

MERCURY.

Summary.

Mercury is found as the sulphide from which it is extracted by roasting.

It is a bright, silvery white fluid, solidifying at -39°C. , boiling at

357° C., and with a specific gravity of 13.6. The atomic weight of mercury is 200.

Mercury combines readily with sulphur and the halogens, but with oxygen only at high temperatures. Concentrated nitric acid is the only acid that has much action upon it at ordinary temperatures.

Mercury is used in scientific instruments, in the preparation of amalgams for mirrors, and for the extraction of gold.

Mercurous chloride, *calomel*, and mercuric chloride, *corrosive sublimate*, are the two most important mercury compounds. Calomel is used in medicine, and corrosive sublimate is a powerful antiseptic.

Exercises.

1. Write the equation for the extraction of mercury from cinnabar.
2. What properties fit mercury for use in thermometers? in barometers?
3. What common metals would float on mercury? Name those that would sink. How would lead act?
4. Under what circumstances is mercury desirable in the collection of gases? What are its disadvantages?
5. Why do surgeons dip their hands into a solution of corrosive sublimate before performing an operation?
6. What special name is given to the alloys of mercury? Name two, and give a use of each.
7. Calculate the percentage composition of the two chlorides of mercury. What law is illustrated by the composition of these compounds?
8. What would be a simple way of testing a solution for a soluble salt of mercury?

CHAPTER XXVIII.

COPPER AND ITS COMPOUNDS.

280. Occurrence and Ores.—Copper is the only metal which occurs free in large, widely distributed deposits. For this reason, it was the first metal extensively used by man. The copper age followed the stone age. The island of Cyprus was noted in the time of the Romans for its production of copper or Cyprian brass. We obtain the symbol Cu from the Latin name, *cuprum*.

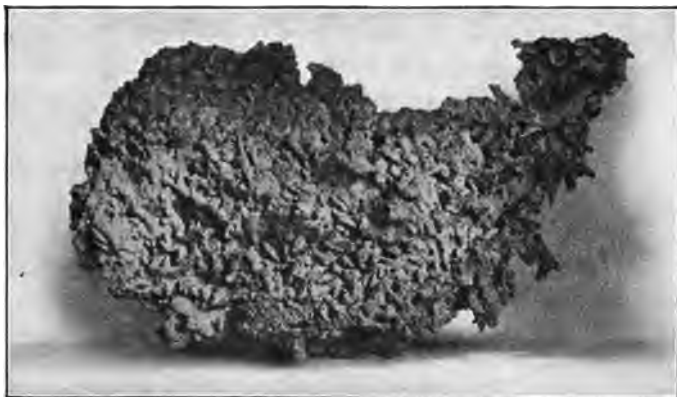


Fig. 101. Mass of native copper (3 x 2 ft.) in the University of Michigan Museum.

The noted mines of native copper in Michigan, along the southern shore of Lake Superior, were extensively worked before Columbus discovered America. From them masses of copper of enormous size, one of which

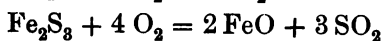
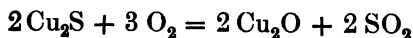
weighed nearly five hundred tons, have been obtained. These mines are still an important source of copper.

The ores of copper are numerous, and many of them have a composition represented by complex formulas; the more important ores besides native copper are sulphides, oxides, carbonates, and silicates. Much copper is obtained from an ore named chalcopyrite, the composition of which corresponds approximately to the formula $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$. Malachite, a basic carbonate of copper ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) is of interest. Polished slabs of malachite often exhibit variegated patterns of different shades of green which are of great beauty, and the mineral is highly valued for ornamental purposes.

281. Metallurgy; Steps in Process. — The metallurgy of copper is complex; not only does the process vary with the kind of ore used, but similar ores are seldom treated in the same manner in different localities. In case the ore contains much chalcopyrite, the process, as carried out by one of the large copper companies, consists essentially in:

1. Roasting a portion of the ore by which sulphur dioxide is obtained and used in the manufacture of sulphuric acid.
2. The production of a complex sulphide called *matte*.
3. Converting the matte into blister copper.
4. Poling the blister copper and casting it into anode plates.
5. Refining by electrolysis.

282. Roasting of Ore and Production of Matte. — When chalcopyrite, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, is roasted, the following reactions may be considered as taking place:



The roasted ore is then smelted in a blast-furnace for the production of matte. A vertical section of one form of blast-furnace is represented in Fig. 102. The crucible (*C*) is the part of the furnace in which the molten matte and slag collect. The body of the furnace consists of two concentric shells (*cs*), made either of wrought iron or of steel, between which cold water (*W*) is caused to circulate to prevent the inner shell becoming heated to a temperature sufficiently high to injure it. Pipes called tuyères (*T*) enter the furnace a short distance above the hearth.

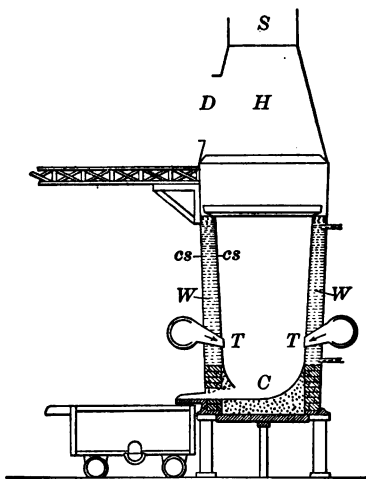


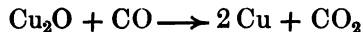
Fig. 102.

They are used to convey a blast of air into the furnace. Above the body of the furnace extend the hood (*H*) and the stack (*S*). A door (*D*), used in charging the furnace, is placed in the hood.

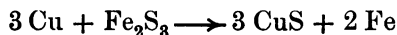
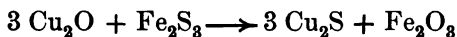
The charge for the furnace consists of the roasted ore mixed with a certain amount of unroasted (green) ore and coke. The ores usually contain considerable silica.

When the furnace is in operation, the blast of air which enters through the tuyères causes a part of the coke to be

converted into carbon monoxide ; this, together with the hot carbon, reduces a part of the cuprous oxide to copper :



As copper has a greater tendency to combine with sulphur than has any other metal present, cuprous sulphide is formed :



A part of the iron unites with the silica which is present in the ore and forms a fusible slag. Some of the iron sulphide remains with the cuprous sulphide and forms *matte*, which is a more or less pure mixture of cuprous and ferrous sulphides. In addition to the sulphides mentioned, matte contains all of the gold and silver present in the ore, and generally arsenic and antimony.

The matte and slag are run into a forehearth, where the lighter slag rises to the top and overflows through a trough, while the matte collects at the bottom and is from time to time drawn off through a pipe. Matte contains from 45 % to 60 % of copper.

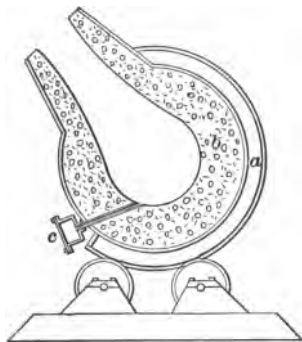


Fig. 103. Converter (sectional).

283. Conversion of Matte to Blister Copper. — Matte is converted into blister copper by means of a process called *Bessemizing*, in a furnace called a converter (Fig. 103). This consists of an iron shell (*a*) lined with a thick layer of a mixture of quartz and clay (*b*). The converter is mounted so that it can be revolved around

a horizontal axis. A blast of air enters through a pipe (c) and is forced through openings near the bottom of the converter. The matte is melted and poured into the converter; then air is blown through the molten mass (Fig. 104). Sulphur, iron, and other impurities are oxidized. Those oxides which are volatile are driven off. The iron oxide, however, unites with the quartz of the furnace lining to form a slag. As sulphur and iron have a greater tendency than copper to combine with oxygen, they are the first to be oxidized. The operator endeavors to stop the blast as soon as the impurities have been removed, and thus prevent the oxidation of the copper. This requires much experience and great skill. The copper obtained still contains all of the gold and silver present in the original ore, and small quantities of other impurities. Molten copper dissolves considerable sulphur dioxide, which is expelled when the mass cools, and gives the copper the appearance which causes it to be called *blister copper*.



By courtesy of *The Scientific American*.

Fig. 104.

Converter in operation.

It would not be advisable to put the blister copper to practical use, since the gold and silver are of too great value to be allowed to remain with the copper. Besides, large quantities of copper are used in the manufacture of electric cables, and small quantities of impurities greatly reduce its conductivity. If the conductivity of pure copper is considered as 100, copper containing 0.8% of arsenic has a conductivity of only 30, and

copper containing 0.5 % of silicon has a conductivity of 28.

284. Poling of Blister Copper and casting of Anode Plates.

—Blister copper is melted in a reverberatory furnace (Fig. 105), and the molten mass is stirred by the gases coming from a long pole or log of green wood, which is forced into the metal. The hydrocarbons dis-

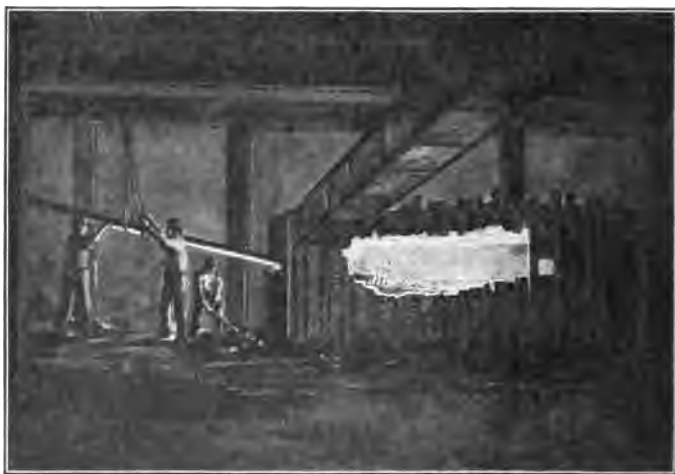


Fig. 105. Reverberatory furnace for poling copper.

tilled from the wood unite with the oxygen combined with the copper. This process is called *poling*, and has for its object the reduction of the small amount of copper oxide present to metallic copper. Any one who has seen the interior of a poling furnace in operation will retain a vivid impression of the seething mass of molten copper, dazzling in its brilliancy of color. After being poled, the copper is cast into anode plates to be refined by electrolysis.

285. Refining by Electrolysis. — The anode plates from the poling furnace are about $\frac{3}{4}$ of an inch thick, 3 feet wide, and 3 feet long. Cathode plates of pure copper about $\frac{3}{16}$ of an inch thick are made by covering a plate of impure copper with a thin layer of grease, and then making it the cathode plate in a bath of copper sulphate.

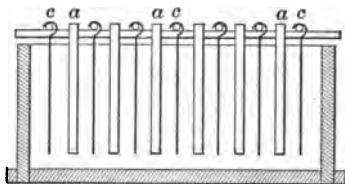


Fig. 106.

a, anodes; c, cathodes.

On the passage of the current, the anode plate dissolves, and pure copper is deposited on the greased side of the cathode plate. The layer of grease prevents the pure copper from adhering firmly to the impure; it can therefore be stripped off and used as a pure copper cathode.

The impure anode plates are connected and arranged as shown in Fig. 106. Some copper refiners do not use pure copper cathode plates, but arrange the impure plates so

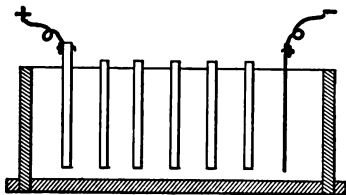


Fig. 107.

that the copper from the front of one plate is deposited on the back of the next one. This arrangement is shown in Fig. 107. At the end of the electrolysis the pure copper is stripped off. In either arrangement the plates are

suspended in wooden tanks containing a warm solution of copper sulphate acidulated with sulphuric acid (Fig. 108). During the electrolysis the bath is kept slowly circulating, and at a definite concentration. When the current passes, pure copper is deposited on the cathode. A part

of the impurities enter the bath, while others, including gold and silver, fall to the bottom of the tank and form a substance known as *mud*. The gold and silver are recovered from the mud.



By courtesy of *The Scientific American*.

Fig. 108. Tank-house for electrolytic copper refining.

286. Properties of Copper. — Copper has a characteristic reddish color. Only two of the common metals, gold and silver, surpass it in malleability and ductility. It stands next to silver as a conductor of electricity.

On exposure to the atmosphere, copper is attacked by carbon dioxide in the presence of moisture, and becomes covered with a coating of a basic carbonate of a greenish color. The coating, once formed, adheres to the copper underneath and protects it. Copper is readily attacked by nitric acid (preparation of nitric oxide, § 168), but neither dilute hydrochloric acid nor dilute sulphuric acid

attack it in the absence of air. It is readily acted upon by hot, concentrated sulphuric acid (preparation of sulphur dioxide, § 139). Boiling concentrated hydrochloric acid slowly converts copper into cuprous chloride, CuCl .

287. Uses of Copper. — Large quantities of copper are used for a great variety of purposes. Among the more important may be mentioned its use as wire and cables for the transmission of electric currents; its employment in the manufacture of various articles for domestic and scientific purposes, such as water-heaters, kettles, stills, vacuum pans, etc. Much copper is also employed in the manufacture of alloys. Brass is an alloy of copper and zinc; bronze, an alloy of copper, zinc, and tin; and aluminum bronze, an alloy of copper and aluminum.

288. Compounds of Copper. — Copper forms two kinds of ions, cuprous, Cu^+ , and cupric, Cu^{++} . Its valence may therefore be considered to be sometimes one and at other times two. The monocuprion unites with negative ions to form cuprous compounds, while the dicuprion unites with the negative ions to form cupric compounds.

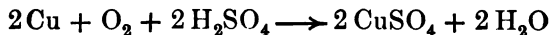
	Oxide	Sulphide	Chloride
Cuprous	Cu_2O	Cu_2S	CuCl
Cupric	CuO	CuS	CuCl_2

289. Oxides of Copper. — *Cuprous oxide*, or red oxide of copper, Cu_2O , occurs in nature. When a strip of copper is heated in air, a layer of cuprous oxide forms under the layer of black cupric oxide. If a mixture of cupric oxide and charcoal is heated, the cupric oxide is first reduced to cuprous oxide, and then the cuprous oxide is reduced to copper. Other reducing agents have a

similar effect on cupric oxide. The formation of cuprous oxide is utilized in testing for glucose by means of Fehling's solution. Fehling's solution contains cupric sulphate, potassium hydroxide, and Rochelle salt. When it is added to a solution containing glucose, or a similar reducing agent, and the mixture is boiled, cuprous oxide separates as a red precipitate. The Rochelle salt is added to prevent the formation of cupric oxide, which, being black, would hide the color of the cuprous oxide. Cuprous oxide is used to give a beautiful red color to pottery.

Cupric oxide, or black oxide of copper, CuO , can be prepared by heating copper in air and also by heating cupric hydroxide, nitrate, or carbonate. Many compounds containing hydrogen are oxidized when heated with cupric oxide, the hydrogen being converted into water. If carbon is present, it is converted into carbon dioxide. These facts make cupric oxide a valuable substance to use in the determination of the quantity of hydrogen and of carbon present in compounds containing these elements.

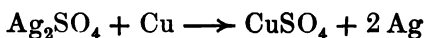
290. Preparation of Copper Sulphate. — Crystallized copper sulphate, or blue vitriol, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, is prepared on a large scale by placing coarse copper shot in a perforated lead basket, and then causing the basket and contents to move up and down so that they will at one time be in the air and at another time immersed in warm, dilute sulphuric acid. When the basket enters the acid, air is carried into it with the shot. The action of the acid on the copper in the presence of air results in the formation of copper sulphate, which passes into solution:



The solution, after being sufficiently concentrated, is

allowed to stand in lead-lined vats in which are suspended lead strips. Blue vitriol crystallizes on the lead and is purified by recrystallization.

Blue vitriol is also obtained as a by-product in one method used in separating gold from silver. The melted alloy of these two metals is granulated by pouring it into cold water. The granulated mass is boiled with concentrated sulphuric acid until the silver is dissolved as silver sulphate. The gold remains undissolved and settles to the bottom of the vat. The solution of silver sulphate is removed to lead-lined vats and the silver separated by the addition of copper:



291. Properties and Uses of Copper Sulphate. — Copper sulphate forms deep blue crystals (Fig. 109) which effloresce in dry air. Its water solution gives an acid reaction with litmus (§ 122).



Fig. 109. Mass of copper sulphate crystals.

For some time the great value of copper sulphate as a fungicide has been recognized. A mixture of copper sulphate and slaked lime, known as the Bordeaux mixture, is now extensively employed for this purpose. A thick paste of calcium hydroxide and copper sulphate was first used near the city of Médoc, France, to keep boys from stealing grapes. When placed upon the trellises and vines

it was conspicuous, and was believed to be poisonous. In 1882, Millardet, professor of botany in Bordeaux, visited the vineyards near Medoc, and was informed by the grape growers that portions of the vineyard which had been treated with the paste were not attacked with mildew. Much work has been done in the United States Department of Agriculture in determining the value of the Bordeaux mixture as a general fungicide. Its use in this country has saved crops worth many thousands of dollars.

Dilute solutions of copper sulphate are used to moisten seeds of cereals prior to sowing, to prevent the attack of fungi called smuts.

Plants known as algæ grow abundantly in the water of ponds and reservoirs. Some of them impart to the water disagreeable odors; others produce effects equally undesirable. Copper sulphate is added to the water of ponds thus affected, in the proportion of one part of copper sulphate to from one to eight million parts of water, for the purpose of destroying algæ. The solution is too dilute to kill fish. The copper sulphate appears to react with the albumen of the algæ to form an insoluble substance which sinks to the bottom of the ponds.

Copper sulphate has many other important uses. It is employed in batteries, in electroplating, as a mordant in dyeing, and for making other compounds of copper.

Summary.

Copper occurs as metal; this and the sulphides are its principal sources.

It is separated from its ores by burning out the sulphur and reducing the oxide by carbon. It is purified by electrolysis.

The atomic weight of copper is 63.6; its specific gravity is 8.9, and its melting point is 1065° C.

Copper is durable under ordinary atmospheric conditions, and is used for protective coverings. Being ductile and a good conductor, it is used for electric conductors. As a constituent of many alloys, copper finds wide use.

Copper sulphate is the most important compound of copper. It is used as a fungicide, for paints, for plating, and in some batteries.

Exercises.

1. What metals are usually found associated with copper?
2. How is iron separated from copper? how is silver?
3. What copper compound is used in pottery and in glass?
Why?
4. What is the result of the action of atmospheric agents on copper?
5. Name three alloys of copper and their constituents.
6. Heavy electric cables often have iron wire above them to which they are fastened. Why?
7. How could you tell whether or not a given substance is a compound of copper?
8. What would be obtained if ammonia were passed over heated copper oxide?
9. State two uses for copper sulphate.
10. How could you tell whether a given substance was gilt (brass) or gold?

CHAPTER XXIX.

SILVER, GOLD, AND PLATINUM.

SILVER.

292. Occurrence. — Silver is the most common of the precious metals. Silver was known and valued from the earliest times, as it frequently occurs free in rocks and is easily separated.

Native silver is found in Arizona, Mexico, South America, and elsewhere, but much of the silver now used is obtained from sulphide ores, usually associated with lead, copper, arsenic, and gold. Silver chloride (horn silver) occurs in nature, and traces of silver compounds are found in sea water. The principal supply of silver is from the United States, Mexico, Australia, and Germany.

293. Metallurgy. — Some of the ores of silver are so complex that various processes are employed in the separation of the metal, but since so large a proportion of the commercial metal is obtained from lead ores, only the method used for these (Parkes' process) will be described.

The ore, largely lead sulphide, is roasted to remove sulphur, and then reduced as described under the metallurgy of lead (§ 349). The crude metal is heated in a reverberatory furnace and stirred. Such metals as copper, antimony, and arsenic are oxidized, forming a scum on the surface of the lead, and this is skimmed off. The molten metal is now run into iron pots and a small

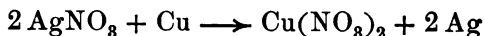
percentage of zinc is stirred into it. As the mixture cools, an alloy of zinc with silver and gold comes to the top and is skimmed off, but little of the lead being removed. If there is much silver in the crude lead, the treatment with zinc may be repeated.

The skimmings containing zinc, lead, silver, and gold are now heated in a retort and the zinc removed by distillation.

The residue, containing lead, silver, and gold, is then heated, *cupelled*, in a shallow furnace exposed to the air. The lead oxidizes, and the melted lead oxide flows off and is recovered. The melted silver and gold remaining is then poured into moulds. A small cupellation furnace is shown in Fig. 110; *a* is the muffle and *b* the cupel in which the silver or gold is finally left as a metallic button.

The gold is separated from the silver by treating the alloy with hot concentrated sulphuric or nitric acid. The silver dissolves as the sulphate or the nitrate, but the gold is not affected, and after washing is melted and cast into bars.

The silver is recovered from the solution by hanging in it plates of copper :



The silver is deposited in a fine crystalline form known as *cement silver*.

Another method of separating gold from silver is by electrolysis. The alloy is made the anode in a dilute nitric acid solution of silver nitrate, the anode sheet being enclosed in a canvas bag. With a current of low voltage,

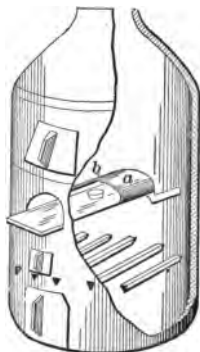


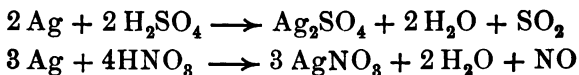
Fig. 110.

silver is dissolved from the anode as the nitrate and redeposited on the cathode as practically pure metal. The gold is unaffected and remains at the anode, and as the anode disintegrates, collects as a mud in the canvas bag.

294. Physical Properties.—Silver is a white metal, fairly hard, capable of receiving and retaining a high polish. It is the best conductor of heat and of electricity. Being ductile and malleable it is readily worked into various shapes.

295. Chemical Properties.—Silver does not change in air, but darkens readily in the presence of sulphur compounds, showing such stains as are seen on silver spoons that have been used with eggs or mustard, on coins carried in the pocket, or on silverware about the house.

Silver does not oxidize on being heated. Alkalies do not affect it. Nitric and sulphuric acids react with it as they do with copper :



296. Uses.—Since pure silver is not hard enough to stand the wear and tear of constant use, it is alloyed with other metals, for instance copper. The silver coins of the United States contain 90 % of silver and are said to be 900 fine. British coins are 925 fine, and this is the grade known as sterling silver. On account of its durability and lustre it has long been used for jewellery and ornaments. An amalgam of silver is often used by dentists, and silver is used on the back of glass for mirrors, and as a plating on cheaper metals.

Some mirrors are made by depositing a layer of silver on

the polished glass. A solution of silver nitrate to which has been added some ammonia and a reducing agent is flowed over the glass and gently warmed. The silver is reduced and deposited as a bright film on the glass. This is washed, dried, and varnished to protect it.

Silver plating is usually done by electrolysis. To secure a firm, uniform deposit, the electrolyte is a solution of silver and potassium cyanides (Fig. 111, *b*) made by adding potassium cyanide solution to a solution of silver nitrate until the precipitated silver cyanide is dissolved. A bar or sheet of silver is used as the anode (*a*) and the object to be plated as the cathode (*c*), a rather weak current being employed. The positive silver ions are discharged and deposited on the cathode. The negative ions, discharged on the anode, combine with the silver, forming silver cyanide. This, on dissolving, is dissociated. The amount of silver in the solution is unchanged, for silver is dissolved from the anode and deposited on the cathode.

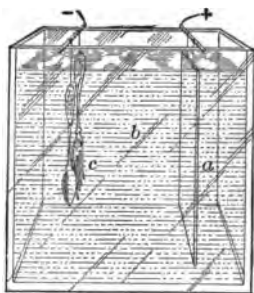
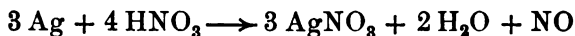


Fig. 111. Silver plating.

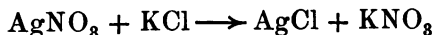
297. Compounds of Silver. — *Silver nitrate*, AgNO_3 , is the most common compound. It is prepared by dissolving silver in nitric acid:



It is very soluble in water and crystallizes from it in flat, rhomboidal, transparent forms. In contact with organic matter and exposed to the light, it darkens. Moulded into sticks, silver nitrate is used as a cauterizing agent for warts, wounds, and sores, and is known as lunar caustic.

Silver nitrate is the most important compound of silver because most of the other silver compounds are made from it.

Silver chloride, AgCl , is made by adding a solution of a chloride to a solution of silver nitrate:



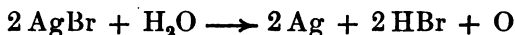
The silver chloride separates as a white, curdy, insoluble solid. Silver chloride does not dissolve in acids, but dissolves in ammonia and in sodium thiosulphate, the *hypo* of the photographer.

Silver bromide, AgBr , and *silver iodide*, AgI , resemble the chloride; they have a yellowish tinge, and are more easily changed in the light and are less soluble. Like the chloride, they are extensively used in photography.

298. Photography.—The preparation of the photographic negative involves these processes: the exposure, the development, the fixing, and the washing. The photographic plate consists of glass or transparent celluloid coated with a film of gelatine containing very finely divided silver bromide, which, as we have stated, is *sensitive* to light in that it becomes somewhat less soluble and *more easily reduced*. In the camera the plate is exposed to light, and the change in the silver bromide is produced, strongly where the light is bright, less intensely in the shadows. The exposure is very short in the camera, and produces no visible change in the plate.

The next operation is to *develop* the picture. As the exposed silver compound is a little more easily affected than the unexposed compound, it is possible to change the one without materially affecting the other. For this, the *developer* is used. The developer is a reducing agent of such strength that it is capable of continuing the change

begun by the light, but is not capable of initiating the change in the unaffected parts of the plate. Ferrous sulphate, pyrogallol, hydroquinone, and many other reducing agents are used as developers to reduce the silver compounds to metal :



The acid is neutralized by the alkali added in the developer, and the oxygen removed by the reducing agent. Where the plate has been exposed to the light, there will be a deposit of silver, which appears dark because it is very finely divided. Where no light acted, the silver compound is unchanged.

When it is seen that the picture is developed sufficiently, it is placed in the *fixing bath*. This is a solution of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, commonly called hyposulphite of soda, and is capable of dissolving many silver *compounds*, such as the silver bromide, which remains unreduced in those parts of the picture where the light has acted least. This unchanged silver bromide is dissolved, and the glass remains *clear* in these places. As all the material sensitive to light has been removed, the plate is said to be *fixed*; it is then thoroughly washed and dried.

On the fixed plate, those parts of the scene which are brightest, that is, those parts which are white or blue, are represented by a dark deposit of silver; the dark parts of the scene are clear, so that shades are reversed; hence it is called a *negative* (Fig. 112, *b*).

The finished picture on paper is made from the negative. The paper is *sensitized*, as was the plate, by a film of silver chloride or bromide. It is exposed to the light under the negative. Now those parts of the paper under the clear parts of the negative will be affected most by the light and

will be the darkest on reduction; the parts under the heavy deposits will be little affected and appear light, as they do in the object, so that the print, being the reverse of the negative, is a *positive* (Fig. 112, *a*), in that its shades agree with those of the object.

The positive may be developed in the same manner as the negative, but in many cases, as *printing out* papers, the developer is in the paper, or film, so that the reduction occurs and the picture appears during the exposure. The

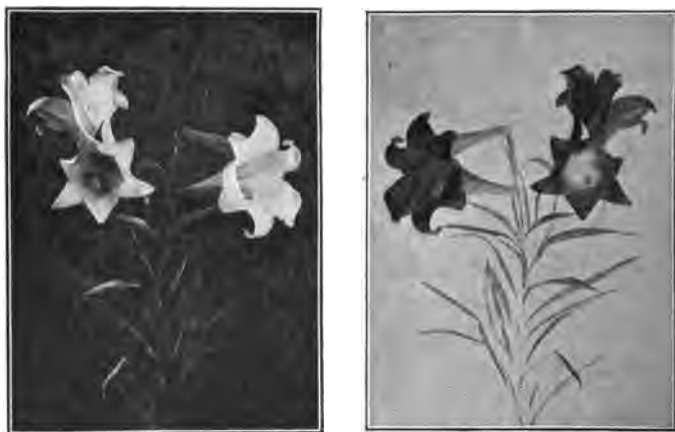


Fig. 112.

a, Positive.*b*, Negative.

print is fixed and washed as the plate was, and to render it more permanent and to improve the color, the print is *toned* by immersing it in a solution of gold chloride, so that some of the silver of which the picture is composed is replaced by gold, giving it a warmer tone. Platinum and lead compounds are also used in *toning*. A melanotype or tinfo is a whitened negative on a polished black surface. Other materials might be used besides silver compounds,

but these are the most sensitive to slight variations in light and are the most easily controlled.

Ferrotypes, or *blue prints*, are the simplest substitutes for silver printing papers. The paper is coated with a mixture of a ferric salt, a reducing agent, and potassium ferricyanide, which has been applied and dried in the dark. On exposure to light, some of the ferric salt is reduced to the ferrous compound, so that when the paper is immersed in water, an insoluble blue is formed where it has been exposed to the light. Where it has been protected from the light, the materials are unchanged, and are removed in the washing.

GOLD.

299. Occurrence and Separation. — Gold has been known from the earliest times. It commonly occurs native, or alloyed with silver and other metals. It also occurs combined with tellurium, an element closely related to sulphur. Native gold is found in veins running through quartz rock and also in the beds of streams whose sands have been formed from the disintegration of such gold-bearing quartz. It often occurs in nuggets varying in size from that of a tiny pebble to a mass weighing over a hundred pounds.

From river sands and gravel gold is separated by washing with water, when the lighter rock particles are washed off, leaving the gold. Partially disintegrated rock and coarse gravels are sometimes mined by washing them down with powerful streams of water and causing the resulting torrent to flow through long flumes or troughs, with transverse cleats along the bottom. These retain the heavy gold and permit the soil and gravel to be swept

on. This last process, *hydraulic mining*, is forbidden in many states on account of its destructive effects.

300. Metallurgy.—When gold occurs in veins in massive rock, the rock is blasted with dynamite. The broken rock is crushed to small pieces by powerful iron crushers and is then pounded into fine powder by heavy iron stamps working in iron troughs. Water is kept flowing through these troughs, and the gold and rock leave them as a thin mud. This is caused to flow over silver-plated copper plates coated with mercury. The mercury amalgamates with the gold, and when a sufficient quantity accumulates, the amalgam is scraped off the plates and freed from mercury by distillation.

The gold that escapes amalgamation is extracted by means of potassium cyanide. It is allowed to stand in a weak solution of cyanide exposed to air for days or weeks and a double cyanide of gold and potassium is formed. The gold is precipitated from this solution by zinc or is extracted by electrolysis. This cyanide process is also applied directly to ores poor in gold and to tellurides.

The separation of gold from copper slimes has already been mentioned (§ 285).

301. Properties.—Gold is soft and heavy and is the most malleable and ductile of metals. The presence of a small amount of other metals, however, often makes it brittle. Gold leaf has been made $\frac{1}{250000}$ of an inch thick. Gold leaf transmits green light, while finely divided gold, when suspended in liquids, appears purple by reflected light, and blue by transmitted light.

Gold is unaffected by air or water at any temperature.

Ordinary acids do not act on it, but it is dissolved by *aqua regia*, with the formation of auric chloride, AuCl_3 .

302. Uses. — Pure gold is used as gold leaf. The metal is too soft to be used alone for other purposes and is alloyed with silver or copper. The proportion of gold is always indicated by the number of carats fineness: pure gold is 24 carats fine, 18-carat gold contains 18 parts by weight of gold and 6 parts of other metals. The gold coin of the United States is 90 % gold and 10 % copper. Articles are gold plated by an electroplating process with a bath of double cyanide of gold and potassium.

PLATINUM.

Platinum occurs native, alloyed with osmium and iridium, which closely resemble it, and with other metals. The most important deposits of platinum are in the Ural Mountains; it is also found in California, Australia, and a few other places. The separation of platinum from the metals alloyed with it is a complicated process.

303. Properties. — Platinum is a white, lustrous metal, about twice as heavy as lead. It is very malleable and ductile and is infusible except in the oxyhydrogen flame or the electric arc. It absorbs or *occludes* large quantities of hydrogen when hot, with an increase in temperature, and releases it on cooling. It does not absorb oxygen when hot, but condenses it on the surface when cold. It may be obtained as a fine black powder, *platinum black*, by the action of a reducing agent on a solution of one of its salts and as a *spongy platinum* by igniting the double chloride of platinum and ammonium. Both of these forms of platinum act as powerful catalytic oxidizing

agents on account of the large surface they possess in proportion to their mass.

Platinum is not attacked by air or water at any temperature, and is not affected by acids, except *aqua regia*. Caustic alkalies, phosphorus, silicon, and carbon attack it when hot, so none of these substances should be heated in platinum vessels. Platinum should never be heated in a smoky flame, on account of its tendency to form a carbide, nor should metals be heated in platinum vessels.

304. Uses. — The infusibility of platinum and its chemical indifference toward the great majority of elements and compounds render it invaluable in chemical operations. It finds extensive use in the laboratory, in dishes, wire, and foil. On account of its cost, which is more than that of gold, it is used only to a limited extent in chemical manufactures. The great expense, however, is partly compensated for by its indestructibility. It is used for stills for the concentration of sulphuric acid, and large quantities of platinum black are employed as a catalytic agent in the manufacture of sulphuric acid by the contact process. It is a good conductor of electricity and expands with heat at the same rate as glass. On account of these properties it is used to connect the filaments of incandescent lamps with the wires outside the exhausted bulbs. The power of platinum to cause the ignition of inflammable gases mixed with air is utilized in self-lighting burners and mantles. Its alloy with iridium is hard and unalterable in air and is used for the manufacture of government standards of length.

305. Compounds of Platinum. — The most important platinum compound is *chlorplatinic acid*, H_2PtCl_6 , which

is formed by dissolving platinum in *aqua regia*. This forms chlorplatينات with metallic compounds. It is used in toning platinum photographs and as a test for potassium compounds. The test depends upon the fact that potassium chlorplatinat is but slightly soluble in water or alcohol, while the corresponding sodium compound is decidedly soluble.

Summary.

Silver occurs native, and with other metals in complex sulphides and as the chloride.

It is extracted from lead bullion by means of zinc, and purified by electrolysis or treatment with acid.

Silver has a specific gravity of 10.5. It is the best conductor of heat and electricity.

Silver is unaltered by pure air, but is tarnished by sulphur compounds.

Silver is alloyed with copper for most uses. A double cyanide of potassium and silver is used for electroplating.

Silver nitrate is made by dissolving silver in nitric acid. It is the basis of other silver compounds.

The *silver halides* are insoluble compounds, and are made more easily reducible by the action of light. *Photographic plates* are coated with silver bromide, which after exposure to the light can be reduced by a developer. The unreduced silver bromide is dissolved by sodium thiosulphate.

Prints are made by exposing to light, under the negative, paper coated with silver bromide or chloride. Toning is the replacement of the deposited silver of the print by gold or platinum, by means of a chloride solution.

Exercises.

1. Why does not silver occur as the oxide ?
2. Why is not silver commonly used as an electric conductor ?

3. Does coating glass with silver or with tin amalgam produce better mirrors? Discuss.
4. How could silver be cleaned that was so tarnished as to resist ordinary silver polish?
5. What is horn silver? "hypo"? sterling silver? lunar caustic? oxidized silver?
6. Give the action of the developer, the fixing bath, and the toning solution in photography.
7. How much silver nitrate can be made from a dime weighing 2.45 grams?

CHAPTER XXX.

ALUMINUM AND ITS COMPOUNDS.

306. Occurrence. — Aluminum never occurs in a free state, although it is one of the most abundant and widely distributed elements. Emery, corundum, ruby, and sapphire are more or less pure forms of aluminum oxide. Clay and the rocks by the decomposition of which it is formed consist chiefly of aluminum silicate. Two minerals of great importance in the preparation of metallic aluminum are bauxite, a hydrate of aluminum, and cryolite, a fluoride of sodium and aluminum.

307. Preparation. — The only process used at present for the extraction of aluminum is an electrolytic one. The electrolyte consists of a solution of aluminum oxide in melted cryolite. The mineral bauxite is used to furnish the oxide. The cryolite is fused and kept liquid by the heat generated during the passage of the current; the aluminum oxide is dissolved by the cryolite and decomposed by the current. The aluminum collects as a molten mass in the bottom of the melting pot; the oxygen is liberated at the anodes, which are oxidized by it.

The apparatus consists of a rectangular iron box, lined with a thick layer of carbon which constitutes the cathode (Fig. 113, *b*). The inside dimensions are approximately $4\frac{1}{2}$ feet long, $2\frac{1}{2}$ feet wide, and 6 inches deep. Carbon rods about 3 inches in diameter and 18 inches long, placed in rows and supported by copper rods, serve as the anodes

(Fig. 113, *a*). These are so arranged that they can be lowered into the bath. The aluminum is allowed to run

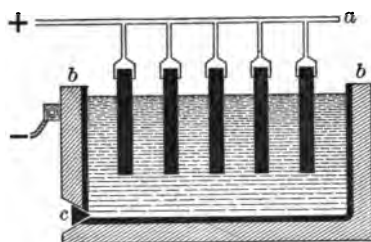


Fig. 113.

off at the base from time to time. The process is made continuous by the addition of fresh supplies of bauxite as needed. A shunt connects the circuit with an incandescent lamp. The resistance of the bath increases as the oxide is decomposed.

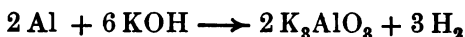
When more aluminum oxide should be added to the bath, the current through the shunt becomes strong enough to make the light glow brightly, and thus notifies the attendant that the bath needs aluminum oxide. A layer of fine coal, which covers the bath, facilitates the addition of the oxide and shields the eyes of the workmen.

308. Physical Properties. — Aluminum is a silver-white metal, capable of a high polish. The dull surface usually seen is the result of a thin coating of the oxide. It is lighter than any other of the common metals, having about the same density as glass. It is malleable and ductile, but not very tenacious. It ranks next to silver and copper in thermal and electrical conductivity.

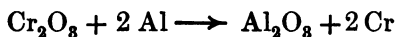
309. Chemical Properties. — Pure aluminum is practically unaltered in air. When aluminum powder or foil is strongly heated, it burns with a very brilliant light, resembling that of magnesium, and liberating a great deal of heat.

Aluminum is scarcely affected by nitric acid at any temperature. Dilute sulphuric acid acts very slowly

with aluminum, with the liberation of hydrogen. With the concentrated acid it behaves somewhat like copper, liberating sulphur dioxide. It reacts with hydrochloric acid, forming aluminum chloride. Aluminum is also dissolved by sodium and potassium hydroxides, with the formation of the corresponding aluminates and the liberation of hydrogen.



310. Uses. — Aluminum has a wide range of uses, although the marked influence of a small amount of impurities has made its application more restricted than was thought probable at one time. Powdered aluminum is extensively used as a paint to protect other metals from corrosion. Aluminum foil is replacing tin foil to a considerable extent. Many small useful and ornamental articles are made of aluminum. It is difficult to solder, so the parts of the larger articles are commonly welded together. Aluminum cooking utensils, when made of the pure metal, prove very satisfactory. When plated with platinum, aluminum proves useful for many purposes in the laboratory, as for evaporating-dishes. Aluminum has a very important use in removing the last traces of oxygen from molten iron. When a mixture of aluminum powder and an oxide of manganese, chromium, or iron is ignited, a rapid combustion and a very high temperature result. This fact is utilized in softening iron for welding and in the production of metallic manganese and chromium:



Aluminum is being used to a considerable extent in place of copper as an electric conductor. An aluminum wire, though larger than a copper wire of the same con-

ducting power, is lighter and does not produce so great a strain on its supports.

Aluminum forms *alloys* with many of the metals. The most important is the alloy with copper, called *aluminum bronze*. It is hard, elastic, unaltered in air, easily cut, and has a color closely resembling gold. It has been successfully used in place of steel for small objects, such as watch-springs and ball-bearings. *Magnalium* is the trade name for an alloy of aluminum with magnesium and other metals. The metals used with aluminum and their proportions vary according to the use to be made of the alloy. It always contains 90% aluminum and less than 2% magnesium. The tensile strength of magnalium is much higher than that of aluminum, and it can be turned in a lathe. It is less corroded by air than aluminum, copper, zinc, or brass. On account of its superior strength this alloy is replacing aluminum for many purposes.

311. Aluminum Oxide.—The occurrence of this compound, Al_2O_3 , as corundum and emery has already been mentioned. It is easily formed as a white, amorphous powder by igniting the hydroxide. It may be prepared in crystalline form by fusing it with lead oxide. The ruby and sapphire can be artificially prepared by adding small quantities of other salts; potassium dichromate gives the ruby color, and a trace of a cobalt compound produces the sapphire blue. The latter fact is used in testing for aluminum. The substance to be tested is first strongly heated with a blowpipe on charcoal to reduce it to an oxide. It is then moistened with a solution of cobalt nitrate and heated; the appearance of a blue color indicates that the substance contains aluminum.

Emery, on account of its great hardness, is extensively

employed as an abrasive for grinding and polishing. An artificial corundum, made by fusing bauxite in an electric furnace, makes a better abrasive than the natural emery and is manufactured and sold under the name of alundum.

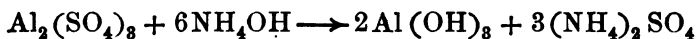
312. Alums.—The first alums known were double sulphates of an alkali metal and aluminum; now similar compounds containing iron or chromium instead of aluminum are called alums. The most common alums are potassium alum and ammonium alum; the composition of the former is represented by the formula, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; ammonium alum is $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

On being heated, the alum gives up its water of crystallization and is converted into a glassy mass known as burnt alum. The alums are much more soluble in hot than in cold water, and are deposited from a cooling solution in well-marked crystals, usually octahedral or cubical in form.

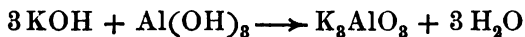
Alum is used for a styptic and in the preparation of aluminum hydroxide, for use in mordanting cloth and in clarifying water.

ALUMINUM HYDROXIDE.

313. Preparation.—This is prepared by the addition of ammonium hydroxide to a solution of an aluminum compound. For example:



Calcium hydroxide may also be used. If sodium or potassium hydroxide is employed, they react in excess with aluminum hydroxide, forming aluminates and water:



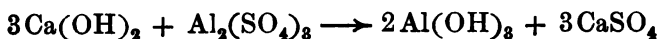
Aluminum hydroxide is a starchy, translucent substance, insoluble in water. It reacts with acids, with the formation of the corresponding aluminum salts; with strong bases, it has, as we have just seen, the action of an acid. On heating, aluminum hydroxide is converted into aluminum oxide:



314. Mordants and Lakes.—The gelatinous character of the hydroxide renders it valuable in dyeing and water purification. Dyestuffs do not readily enter the fibre of cotton goods, so it is necessary to use some substance to cause the dye to adhere and prevent it from washing off. Such a substance is called a *mordant*. It is found that when aluminum hydroxide is precipitated in a solution containing coloring-matter, the color is carried down by the hydroxide as it settles, leaving the solution clear. The mixture of the color and aluminum hydroxide is called a *lake*; lakes are used in dyeing and as pigments. In dyeing cotton, aluminum hydroxide is precipitated on the fibre, either by soaking the cloth first in alum and then in ammonium hydroxide solution, or by impregnating it with aluminum acetate, which yields the hydroxide on heating. The cloth, mordanted with aluminum hydroxide, is soaked in the dye, which forms an insoluble lake with the mordant, and thus produces a fast color. Other gelatinous hydroxides, as those of iron and copper, are used as mordants. Many mordants react chemically with the dye, producing new shades. So it is possible, by the use of the proper mordants, to secure different colors from the same dye. This is done in calico printing, where the pattern is first stamped with a mordant. When the cloth is passed through the dye, the mordanted portions take it up and

retain it, while the color is removed from the unmordanted parts by washing.

315. Coagulum in Water Purification. — The use of aluminum hydroxide in water purification is similar to that in dyeing ; it carries down with it suspended particles of foreign matter. The hydroxide is produced in this case by adding proper proportions of aluminum sulphate and lime :



The aluminum is completely removed by precipitation ; the precipitate carries with it the greater part of the sediment and disease germs. The calcium sulphate is partly precipitated and partly dissolved, adding to the hardness of the water. In water containing a considerable amount of calcium bicarbonate in solution, this salt is sufficient to precipitate the hydroxide ; in such cases aluminum sulphate or alum is added to the water and the precipitation takes place without lime.

ALUMINUM SILICATES.

316. Clay and Pottery. — Ordinary clay is an impure silicate of aluminum formed by the decomposition of felspathic rock. Felspar is a silicate of aluminum and an alkali metal. When such rock is exposed to the action of the weather, the alkali silicate is removed by the water and carbon dioxide, and the residue left is *kaolin*, or clay mixed with other rock materials, as sand and mica. Pure kaolin is a white, pulverulent mass ; when wet, it is plastic and can be moulded. When the moulded clay is heated and dried, it shrinks. Iron compounds often give clay a red color, seen in some bricks and in roofing and drain tiles. Light brick is made from clay containing little or

no iron. Clay containing silica is used for firebricks, stove linings, and crucibles.

Bricks, earthenware, porcelain, and china are made by moulding the clay into the desired form and baking in a furnace or *kiln*. In making common earthenware articles, the baking temperature is not very high and the mass is porous, as in flower pots. In making roofing tiles, jugs, and drain pipes, salt is thrown into the fire; it volatilizes and forms on the surface of the articles a glaze impervious to water, consisting of a fusible silicate of sodium and aluminum.

Stone ware, granite ware, and crockery are made from purer varieties of clay and are more carefully moulded. In addition to the clay, they contain some fusible, hardening material. A heavier and more durable glaze is used than that on earthenware.

Porcelain and china are made from pure kaolin, felspar, and quartz. The materials are ground fine, thoroughly

mixed and wet. The wet mass is then modelled or moulded in plaster of Paris moulds and dried; when dry enough to handle, the mould is removed and the article smoothed. It is then *fired* at a low temperature which leaves it firm and hard, but porous and ready for the glaze.

This consists of felspar

and quartz ground fine and suspended in water. The article is dipped into the mixture and dried. It is then placed in a *seggar* or fire-clay box (Fig. 114, *b*) and sup-

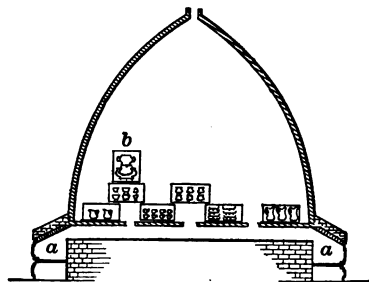


Fig. 114. Pottery Kiln.

a, Fire-box; *b*, Seggars.

ported on a tripod in such a way that it shall not touch the box. This is placed in the oven, the temperature of which is raised to a red heat in from twelve to twenty-four hours. The temperature is then increased for three days or more, and then allowed to fall very slowly. The mass is then hard, dense, white, translucent, thin, and not easily affected by chemicals, except alkalies. The colors that are used in decorating china are composed of substances that are stable at the high temperature necessary for fusion of the glass.

317. Cement and Concrete.—Hydraulic cement results from the heating of a mixture of limestone and clay until they just begin to melt together. Many natural limestones contain the aluminum silicate mixed with the calcium carbonate in nearly the required proportions. Such cement rocks, when burned in a manner similar to that used in making quicklime, yield natural cements. Artificial cements are made by grinding clay or shale with marl or with limestone, then burning and powdering.

Cement is believed to consist of a mixture of calcium silicate and calcium aluminate. When mixed with water, it forms a mass that solidifies, or *sets*, in a short time. It differs from lime in the fact that it sets under water. After it has set, it slowly increases in firmness and tenacity, requiring months and sometimes years to attain its greatest strength. This process is known as *hardening*. The chemistry of the hardening of cement is not very well understood, but it is thought to be due to the formation of crystals by the absorption of water of crystallization. The compounds in the hardened cement are probably a hydrated silicate and aluminate of calcium, of different composition from those found in the dry cement.

The chief use of cement is in making concrete, a mixture of cement, sand, and broken stone. Concrete is used in the construction of buildings for the foundations, floors, and walls by pouring the wet concrete into troughs of board, around twisted rods of steel set in the centre of the trough and parallel to its sides (reënforced concrete). It is indispensable for bridge piers and other structures below the water. It is also extensively used in sidewalks.

Summary.

Aluminum does not occur native. Its oxides and silicates are found widely distributed.

It is prepared by the electrolysis of oxide of aluminum dissolved in cryolite.

Aluminum is a silver-white metal; specific gravity, 2.6; melting-point, 660°. It is a good conductor of electricity.

Aluminum dissolves in hydrochloric acid and in potassium hydroxide.

It is used for making aluminum bronze, cables for conducting electricity, paint, flashlight powders, foil, ornamental articles, and cooking utensils.

Corundum, ruby, and sapphire are nearly pure *aluminum oxide*. Emery is corundum mixed with iron.

Common (potash) *alum* has the formula $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$.

Aluminum hydroxide possesses the properties of a base and those of an acid.

It is used as a mordant and in the purification of water.

Clay is an impure silicate of aluminum and is used in the manufacture of bricks and earthenware.

Kaolin, nearly pure aluminum silicate, is used in the manufacture of porcelain and china.

Hydraulic *cement* is made by heating to incipient fusion a mixture of limestone and clay. Cement hardens under water.

Exercises.

1. Would you carry on the electrolysis of sodium chloride in an aluminum dish? Would you concentrate a solution of nitric acid in an aluminum vessel? Would you concentrate a solution of potassium hydroxide in an aluminum cup? Explain.

2. For what purposes is aluminum bronze used?

3. Write an equation showing how aluminum hydroxide can play the part of a base; of an acid.

4. How could you show that common alum contains aluminum?

5. What would be the weight of a piece of aluminum containing a cubic foot? A cubic foot of water weighs 62.5 lb.

6. How much calcium hydroxide would be required to combine with 20 kilos of aluminum sulphate?

7. How much aluminum is contained in 200 tons of aluminum oxide?

8. What compound of aluminum is formed when a solution of calcium carbonate reacts with a solution of aluminum sulphate?

9. How many liters of hydrogen would be liberated by the addition of 9 grams of aluminum to an excess of hydrochloric acid?

CHAPTER XXXI.

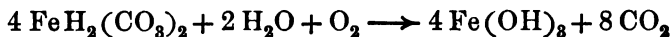
IRON, COBALT, AND NICKEL.

318. Occurrence of Iron. — A consideration of the enormous quantity of iron used annually for an almost unlimited number of purposes, will show how impossible our present civilization would be without this metal.

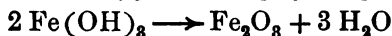
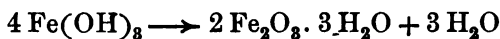
Native iron occurs in igneous rocks in pieces varying in size from small grains to that of a mass found in Greenland which weighed more than a ton. As iron rapidly corrodes when exposed to moist air, native iron is not of common occurrence but compounds of iron are common. The red and yellow colors of soils are generally due to oxides and silicates of iron. Nearly all meteorites contain iron alloyed with nickel. Ferric oxide is found very widely distributed.

319. Formation of Iron Ores. — When water percolates through a soil containing much vegetable matter, it takes up substances capable of reducing ferric compounds to ferrous compounds. When water containing carbon dioxide comes in contact with the ferrous compounds, acid ferrous carbonate, $\text{FeH}_2(\text{CO}_3)_2$, is formed, which is soluble. In this way iron is dissolved out of the soil. If water containing acid ferrous carbonate collects in a warm place *not in contact with air*, carbon dioxide is driven off and ferrous carbonate (siderite), which is insoluble in water, may be deposited. When water con-

taining acid ferrous carbonate is *exposed to the air*, ferric hydroxide is formed.



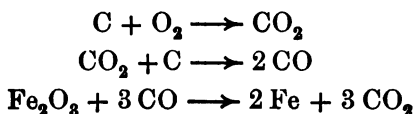
This may be deposited, and on becoming dry may lose sufficient oxygen and hydrogen in the form of water to convert it into hydrated ferric oxide (limonite), $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$, or into ferric oxide (hematite), Fe_2O_3 :



Siderite, FeCO_3 , limonite, $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$, hematite, Fe_2O_3 , and magnetite, Fe_3O_4 , are the most important ores of iron. Pyrite (FeS_2), commonly called fools' gold, is also widely distributed. Large quantities of it are roasted for the production of sulphur dioxide and some iron is smelted from the residue.

320. Manufacture of Cast Iron. — Iron ores are smelted in a blast-furnace which is operated in a manner similar to that employed in the production of copper matte (§ 282). An iron blast-furnace (Fig. 115) consists of a steel shell from 75 to 90 feet in height, lined with a thick layer of fire-brick. Cold water is made to circulate through hollow castings built into the fire-brick just above the tuyères. This portion of the shell surrounds the part of the furnace where the most energetic chemical action takes place during the smelting. The tuyères are pipes through which powerful blasts of hot air are forced. If hematite containing sand is the ore used, the reduction is accomplished in the following way. The ore mixed with the right quantities of limestone (as a flux) and coke (as fuel and as reducing agent) is dropped in at the top of the furnace from time to time. The heated blast of

air forced through the tuyères comes in contact with the burning coke and forms carbon dioxide, which is immediately reduced to carbon monoxide by the excess of carbon. The carbon monoxide reduces the iron oxide to iron:



Simultaneously with the reduction of the ferric oxide, some of the silica is reduced to silicon, and sulphur and phosphorus are reduced. The iron takes up these elements and from 4% to 7% of carbon. This impure iron settles to the bottom of the furnace and is drawn off through a hole as a white-hot stream of molten metal and cast into ingots called *pigs*. The product is known as pig iron or *cast iron*. The flux of limestone, mentioned above, combines with the silica, alumina, and other earthy impurities in the ore, forming double silicates of calcium and aluminum known as *slag*, a glassy substance which remains fluid at the high temperature of the furnace. Both slag and the molten cast iron collect in the crucible, the slag floating on the heavier iron.

The desirability of cheap and rapid production of cast iron has brought the blast-furnace to its present perfection. The opening at the top through which the charging is done is closed by a cup and cone arrangement (Fig. 115). The best modern furnaces sometimes have an air-lock at the top, closed above and below by a cup and cone. In such a furnace the charge can be let into the air-lock, and then, after the opening at the top is closed, can be allowed to drop into the furnace. This method prevents the escape of gas during charging. The gases produced during the smelting, which contain about

20% carbon monoxide, are conveyed away from near the top of the furnace through a large flue. This furnace gas is burned to supply heat for the air-blast and under the boilers to generate steam for the engines which compress the air for the tuyères.

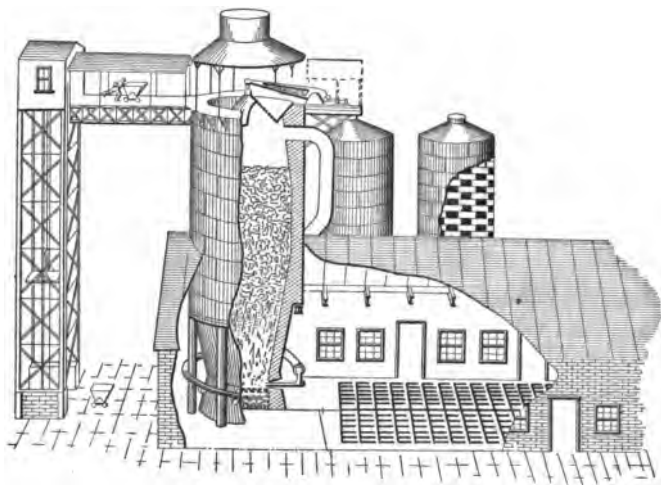


Fig. 115. Blast Furnace for Manufacture of Cast Iron.

The crucible in which the molten iron and slag collect is about 16 feet in diameter. Holes are drilled through its sides for the removal of slag and iron. The process is called tapping the furnace. As soon as the iron or slag has been removed, the tap-hole is closed by a clay plug which is instantly hardened by the heat. The slag is tapped off about every two hours, and the iron every four to six hours. From 70 to 120 tons of metal are drawn off at each cast. If the iron is to be used in making steel in works near by, it is often carried directly there in large ladles; otherwise it is run into pigs.

321. Composition and Properties of Cast Iron. — If the iron, after being drawn from the blast-furnace, is suddenly cooled, a white cast iron is obtained. The carbon in this is in chemical combination with the iron as iron carbide, Fe_3C . When the molten iron is cooled slowly, most of the carbon separates in the form of graphite, and the product is known as gray cast iron. As iron carbide is a very hard compound, white cast iron is harder than the gray variety.

Cast iron always contains considerable carbon (4% to 7%) and is the most easily melted form of iron. It expands when it passes from a liquid to a solid. Therefore, when molten cast iron is poured into a mould, and allowed to solidify, the metal readily takes the shape of the mould. Phosphorus and sulphur make cast iron brittle. Cast iron is not malleable and can be neither welded nor tempered. It is used for casting articles, such as stoves and ornamental iron work, which are not to be subjected to shock. Wrought iron and steel are made from cast iron.

322. Manufacture of Wrought Iron. — Wrought iron is prepared by heating cast iron placed on a layer of ferric oxide in a reverberatory furnace (Fig. 118, p. 353). Flames from the burning fuel play over the bed of the furnace upon which rests the cast iron and oxide. When the mass becomes molten, the carbon, silicon, sulphur, and phosphorus contained in the cast iron are oxidized. The carbon, changed into the monoxide, bubbles off, while the other impurities pass into a slag. The iron becomes pasty because pure iron has a higher melting-point than impure. The molten mass in the furnace is stirred or *puddled* and the pasty iron is gathered into large balls called *blooms*. These are removed from the furnace and nearly freed from slag by a process of squeezing and working under a

trip-hammer. The iron is then rolled so as to give the finished product a fibrous structure. The small portion of slag left in the iron aids in the process of welding.

323. Properties and Uses of Wrought Iron. — Wrought iron is the purest form of commercial iron. Good varieties contain not more than 0.3% of carbon. Piano wire is a form of wrought iron containing less than 0.1% of carbon.

When wrought iron is heated, it becomes plastic before melting. When in this condition, two pieces on being hammered together adhere firmly. The hammering is to force from the joined surfaces the thin coating of iron oxide formed on them in the fire and to insure a close union. This process is called *welding*. Plastic wrought iron can be hammered into various shapes, rolled into bars, and drawn into wire. Wrought iron is tough and can be bent or stretched without breaking. It can very easily be converted into a temporary magnet. Wrought iron is used to make anchors, chains, wire, and other articles which are intended to withstand sudden and severe strains. As wrought iron can be readily forged and welded, it is the iron used by the blacksmith. It cannot be tempered.

324. Bessemer Iron and Steel. — Much cast iron is converted into Bessemer steel, or more properly Bessemer iron. About fifteen tons of molten cast iron are poured into a Bessemer converter (Fig. 116), which is an egg-shaped furnace built of wrought iron plates and lined with a thick layer of refractory material. The bottom is perforated with holes so that streams of air can be blown through the molten metal. The blast lasts from eight to ten minutes, during which the oxygen of the air unites with the silicon, carbon, and other impurities in the cast

iron, leaving nearly pure iron. The heat of combustion raises the temperature of the metal to a high degree, producing what is known as the "boil."

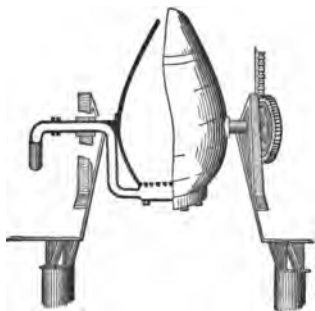


Fig. 116. Bessemer Converter.

Just as the iron commences to burn the blow is stopped, and the desired amount of a cast iron called *spiegeleisen*, which is rich in carbon and manganese, is added. The blast of air is forced through the mass for a short time to thoroughly mix the ingredients. The *spiegeleisen* furnishes the de-

sired amount of carbon, and the manganese unites with any dissolved oxygen present. The oxygen is thus prevented from escaping and producing blow-holes when the mass cools. The manganese also improves the quality of the metal. At the end of the process, the converter is turned over and the contents poured into a ladle and cast.

If the pig iron contains sufficient sulphur and phosphorus to materially injure the quality of the Bessemer iron, the converter is lined with basic material. The calcium oxide formed when this is heated unites with the phosphorus and sulphur, thus removing them from the iron. The use of a basic lining was discovered by Thomas and Gilchrist, and the process is named for them. The slag produced, known as Thomas slag, contains basic phosphates and is of value as a fertilizer.

325. Steel by Open Hearth Process.—Much steel is now made by the open hearth process. An open hearth furnace (Fig. 117) has a large bed (*E*) lined with fire-brick

and sand (*H*) on which the charge is placed. Gas is used as fuel and is heated before entering the furnace by passing through a checkerwork of hot fire-brick (*A*). The heated gas is passed into the furnace through a pipe (*a*), while through another flue (*b*) air enters which has been similarly heated. The object is to obtain a higher temperature than could be obtained by burning cool gas. The burning gas passes over the charge on the furnace bed and the hot, gaseous product escapes through checkerworks

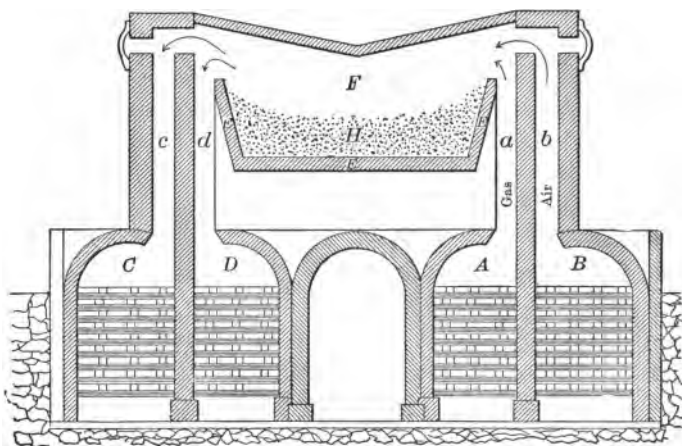


Fig. 117. Open Hearth Furnace.

(*C*, *D*) which are a duplicate of those used to heat the gas and air. One set of checkerworks is thus raised to a high temperature by combustion products, while the other is being cooled as it heats the gas and air about to enter the furnace. About every twenty minutes the direction of the gas and air is reversed by means of a system of valves, so that gas and air pass through the recently heated checkerwork while the flame from the furnace passes through the one just cooled.

The furnace charge consists of scrap steel, pig iron, and iron ore. The scrap steel is placed on the bottom in order to protect it from the oxidizing action of the flame. The manganese and silicon are oxidized by the flame, while the iron ore is active in furnishing oxygen to consume the carbon. The process consumes from eight to twelve hours and is watched and controlled most carefully by the operator. Samples of metal are repeatedly taken from the furnace and examined to determine when the impurities have been removed and the carbon has been reduced to the desired amount. In case the pig iron contains much phosphorus, a basic furnace lining can be used as in the Bessemer process. The steel produced is of much better quality than the metal made by the Bessemer process and is suitable for the manufacture of connecting rods, shafts, armor-plate, heavy ordnance, etc., where great strength and ability to stand vibration are required. It can be forged and tempered. The percentage of carbon varies from 0.6 in soft steel to 2.0 in hard.

326. Crucible and Cementation Processes. — *Crucible steel* is made by heating the best wrought iron mixed with a pure cast iron in a graphite crucible. When pure iron is heated to a temperature above 850° , it is converted into an allotropic form of iron which is capable of absorbing carbon. The carbon at first forms a solid solution with the iron, but after the carbon has reached 0.8 % of the mass, it separates as iron carbide, Fe_3C , forming a homogeneous mixture with the iron. In the manufacture of crucible steel, the heating is continued until sufficient carbon has been absorbed from the crucible to make the desired quality of steel. A very high-grade steel, valuable for the manufacture of edged tools, or springs, is produced in this way.

Steel is made in the *cementation process* by heating wrought-iron bars, packed with fine charcoal, in compartments of fire-brick. The operation is continued at red heat for a week or more and the carbon slowly penetrates the iron. The cementation process, however, is expensive, and is being replaced by the cheaper crucible process.

327. Special Steels.—Certain of the less familiar metals when added in small quantities produce steel of great hardness, toughness, or tensile strength. More than 8% of manganese in a steel, or chromium in smaller amount, gives great hardness to the steel. Tungsten and molybdenum are used for making tools of *self-hardening* steel, which is made without tempering and which retains its cutting edge for a long time. Manganese, chrome, and nickel steels are used for safes, armor plates, and parts of machinery subject to great stress or vibration, as shafts or automobile bearings. Deposits of iron ore which had been regarded as too refractory to work have been made valuable by the demand for these special steels.

328. Hardness and Tempering of Steel.—The hardness of steel depends not only upon the amount of carbon which it contains, but also upon the manner in which it is worked. In general, the more iron carbide (Fe_3C) a steel contains, the harder and more brittle it is. If a hard steel, a homogeneous mixture of iron carbide and iron, is cooled slowly from a red heat, the iron carbide begins to decompose, at a temperature below 670° , into iron and graphite, giving a softer steel. If a steel containing iron carbide is *suddenly cooled* from about 670° , the carbide has not time to decompose, and a hard steel is obtained. If such a steel is now heated to a temperature *less* than that required for

the formation of iron carbide (670°), the latter gradually decomposes into iron and graphite. Hence, the reheating, *provided it is done below 670°* , brings about the same decomposition as the slow cooling mentioned above. Heating for a long time at moderate temperatures, or quick heating to the higher temperatures below 670° , accomplishes the same result, viz. the decomposition of the iron carbide. The process, however, can be stopped at any time by a sudden cooling, and a steel of the desired hardness obtained. The temperature can be estimated by a play of colors ranging from yellow to brown, red, purple, violet, and blue, to gray, which appear when the metal is heated. These colors are due to the formation of thin layers of iron oxide, causing interference colors. The colors follow each other when the metal is cooled, and as soon as the right color is obtained the process is stopped by dipping the article into either water or oil.

COLOR.	TEMPERATURE.	STEEL USED FOR
Pale yellow	430° – 450°	Razors
Full yellow	470°	Penknives
Brown	490° – 510°	Shears and tools for brasswork
Purple	520°	Table knives
Blue	530° – 570°	Watch-springs and sword-blades
Blue-black	610°	Saws and other wood-working tools

The yellow tints give very hard but brittle steels, while, as we proceed toward the blue, the steel is softer but tougher. The films are usually removed by grinding, but are seen on some saws and springs.

329. Classification of Iron and Steel. — Commercial iron is commonly classified as cast iron, wrought iron, and steel. Cast iron contains the highest percentage of carbon,

wrought iron the least, and steel usually stands between. Chemical composition, however, is not a sure way of distinguishing these forms, as some steels contain less carbon than certain wrought irons. Moreover, the condition the carbon is in, whether free or combined with the iron, is as important a factor as its percentage. Knowledge gained from a careful study of the structure of a polished and etched section under a microscope is used more and more as a guide to the true nature of an iron or steel. This and some recent principles developed by physical chemistry have put the iron industry on a scientific basis. At best, the classification of iron is difficult, and unless we classify a product according to the process by which it is made, we shall be confused by the many varieties of steel and iron that grade into one another.

330. Pure Iron.—Pure iron may be prepared by the reduction of pure iron compounds, as the oxalate, in a stream of hydrogen; or electrolytic iron may be deposited from solutions of certain iron salts.

Pure iron is a white, lustrous metal which is very tough and which fuses only at a high temperature. It is malleable, ductile, and may be temporarily magnetized.

In dry air pure iron does not rust, but in moist air rusting proceeds rapidly, particularly if carbon dioxide is present. Iron decomposes water very slowly at ordinary temperatures, but at higher temperatures the reaction proceeds rapidly. With cold, dilute acids hydrogen is evolved and a salt is formed. With hot, or more concentrated acids, certain reduction products may be produced. When cast iron is dissolved in acids, the unpleasant smell is due to the formation of hydrocarbons and to sulphur and phosphorus compounds from impurities in the iron.

IRON COMPOUNDS.

331. Iron forms two kinds of ions,—bivalent, Fe^{++} , and trivalent, Fe^{+++} . Bivalent ions result from the dissociation of ferrous compounds, and trivalent ions from the dissociation of ferric compounds. Compounds in which iron has a valence of *two* are known as *ferrous* compounds; those in which the valence of iron is *three* are termed *ferric* compounds.

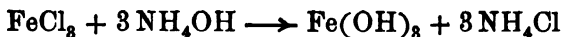
332. Oxides of Iron.—*Ferrous oxide*, FeO , can be prepared by the reduction of ferric oxide with hydrogen or carbon monoxide. It is a black powder which cannot be kept in air on account of the ease with which it passes into ferric oxide.

Ferric oxide, Fe_2O_3 , forms the most important ore of iron. It can be readily prepared by heating ferric hydroxide, ferrous carbonate, or ferrous sulphide. Ferric oxide constitutes the coloring matter of such pigments as Venetian red, Indian red, and light red. When ferrous sulphate is calcined, a form of ferric oxide known as *rouge* is obtained. Rouge is used for polishing and as a pigment. Limonite, or hydrated ferric oxide ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), is found in nature mixed with fine clay and sand. Such mixtures constitute the pigment yellow ochre. When calcined, various shades of yellow, orange, and brown are obtained. These are sold as raw sienna, burnt sienna, raw umber, and burnt umber.

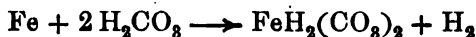
The *magnetic oxide of iron*, Fe_3O_4 , occurs in nature as lodestone. It is formed when ferric oxide is heated to a high temperature and when iron is burned in oxygen or air. It constitutes what is known as blacksmith's scale, formed when red-hot iron is worked. When steam

is passed over red-hot iron, hydrogen is liberated, and a firmly adhering film of magnetic oxide is deposited on the iron. This film prevents the rusting of the iron under it. *Russia iron*, used as a covering for locomotive boilers, etc., is iron which has been artificially coated with magnetic oxide of iron.

333. Hydroxides of Iron. — *Ferric hydroxide* can be formed by the addition of a base to a solution of a ferric salt:



It is a reddish brown compound, which, on drying, changes to iron-rust. *Iron-rust* may be considered as a double compound of ferric oxide and ferric hydroxide. It is probably produced in a manner analogous to that described for the natural formation of hematite. Iron dissolves in water or moisture from the air containing carbonic acid, forming acid ferrous carbonate:

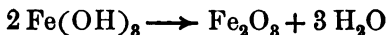


This substance, on drying and further oxidation, is converted into iron-rust. If we represent iron-rust by the formula $\text{Fe}_2\text{O}_3 \cdot 2 \text{Fe}(\text{OH})_3$, the chemical equation would be

$$4 \text{FeH}_2(\text{CO}_3)_2 + \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 \cdot 2 \text{Fe}(\text{OH})_3 + \text{H}_2\text{O} + 8 \text{CO}_2$$

A coating of rust does not protect the iron under it, because the coating does not adhere, but scales off.

When ferric hydroxide is heated to a red heat, it is converted into ferric oxide and water:



Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, appears white when first precipitated, but soon changes to dull green and then to brown, by oxidation.

334. Chlorides of Iron. — *Ferrous chloride*, FeCl_2 , is formed when iron is heated in hydrogen chloride. It is also formed when iron is dissolved in hydrochloric acid in the absence of air. It can be crystallized as a pale green compound, $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$. It is unstable in air.

Ferric chloride, FeCl_3 , can be prepared by passing chlorine over hot iron; by dissolving iron in aqua regia; and by dissolving ferric oxide in hydrochloric acid. When hydrogen peroxide is added to a solution of ferrous chloride containing hydrochloric acid, ferric chloride is instantly formed. Ferric chloride is used in medicine, and in general whenever a soluble ferric salt is required.

335. Sulphates of Iron. — *Ferrous sulphate*, $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, is a by-product in many industries. Scrap-iron is added to sulphuric acid that has been used in the refining of petroleum, or for cleaning iron. The iron is dissolved, and on evaporating the solution, crystals of green vitriol, sometimes called copperas, are obtained. Much ferrous sulphate is used in the manufacture of blue pigments, as a mordant, in the preparation of black inks, and for the precipitation of gold from solutions of its chloride.

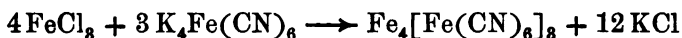
When solutions of ferrous sulphate and tannic acid are mixed, ferrous tannate, a nearly colorless compound, is formed. On exposure to the air, ferrous tannate is changed to ferric tannate, which is insoluble, and has a black color. Ferrous tannate is the chief ingredient of iron inks. As the writing would not at first be visible if a solution of pure ferrous tannate were used, some dye is added to give the ink color. On exposure to the air, ferric tannate is formed, which gives the ink its permanent black color.

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is formed when ferrous sul-

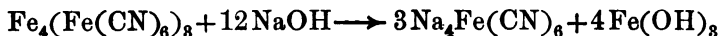
phate is oxidized in the presence of sulphuric acid. It is used with ammonium sulphate in the preparation of ferric ammonium alum, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

336. Ferrocyanides. — On igniting a mixture of nitrogenous organic matter, scrap-iron and potassium carbonate, cooling the mass, and then treating it with hot water, *potassium ferrocyanide*, $\text{K}_4\text{Fe}(\text{CN})_6$, passes into the solution. When the solution cools, crystals of ferrocyanide, or yellow prussiate of potash, separate. These have a composition represented by the formula $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

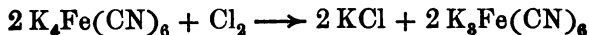
A solution of potassium ferrocyanide does not give the usual characteristic reactions of iron because the iron exists as a part of a complex ion, $\text{Fe}(\text{CN})_6^{--}$. When solutions of ferric salts and potassium ferrocyanide are brought together, a deep blue precipitate, ferric ferrocyanide, or Prussian blue, is formed. The reaction is made use of in testing for ferric ions (Fe^{+++}):



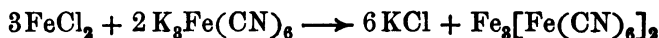
Prussian blue is an important pigment. Blueing, used for laundry purposes, often contains Prussian blue. When the clothes with which it is used are not thoroughly freed from soap, the alkali of the soap decomposes the ferric ferrocyanide, precipitating ferric hydroxide on the cloth and producing spots of iron-rust:



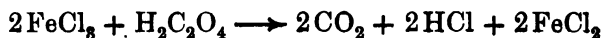
337. Ferricyanides. — *Potassium ferricyanide*, or red prussiate of potash, $\text{K}_3\text{Fe}(\text{CN})_6$, can be prepared by treating a solution of potassium ferrocyanide with chlorine:



Solutions of potassium ferricyanide, when added to those of ferrous compounds, give a blue precipitate, ferrous ferricyanide, or Turnbull's blue :



This compound constitutes the color of the *blue-print*. When a solution containing ferric chloride and oxalic acid is exposed to the sunlight, the ferric salt is reduced to a ferrous salt :



When a sheet of paper is coated in a darkened room with such a mixture, and then dried and exposed under a negative to the sunlight, the greatest reduction will take place where the light is brightest. On covering the exposed paper with a solution of potassium ferricyanide, Turnbull's blue will develop wherever ferrous iron exists, and the depth of color will be proportional to the amount of ferrous salt present. In other words, potassium ferricyanide is in this case used as a developer. The picture can be fixed by washing away the ferric chloride and the excess of potassium ferricyanide.

Blue-print paper is generally coated with a mixture of potassium ferricyanide and ammonium ferric citrate. Such a paper, after exposure, is developed and fixed by washing with water.

COBALT AND NICKEL.

Cobalt and nickel resemble iron in being attracted by a magnet. Their chemical properties are also like those of iron.

338. Cobalt Ores and Extraction.—Cobalt is found as a minor constituent of ores of complex composition. They

are usually sulphides or arsenides, in which iron is the predominating metal, but which contain copper and nickel as well. Cobalt speiss, CoAs_2 , is found in Saxony; cobalt-glance, $\text{CoAs}_2 \cdot \text{CoS}_2$, in Norway and Sweden. The ores are usually worked up to obtain cobalt compounds without separating the element in the metallic state. They are first roasted to remove sulphur and arsenic, and the resulting oxides are then dissolved in acids.

339. Properties of Cobalt. — Cobalt is a hard metal, malleable and ductile, and capable of receiving a high polish. Its melting-point, like that of iron, is high. It dissolves readily in nitric acid, but is acted on slowly by other acids. Solutions of cobalt salts have a rose color. No practical uses have yet been made of metallic cobalt.

340. Compounds of Cobalt. — The chloride, CoCl_2 , and the nitrate, $\text{Co}(\text{NO}_3)_2$, are of some importance. The chloride has a peculiar property of changing its color when exposed to air of varying humidity. These changes are explained by the fact that the substance forms a number of different compounds with varying amounts of water of crystallization which pass readily into one another. The less hydrated forms are blue or lavender, while the more hydrated are red. Heated or exposed to dry air, the red salt loses water of crystallization, and is changed to a blue, less hydrated form. Advantage is taken of this fact to make "sympathetic ink," which is invisible until heated, and for simple apparatus to detect the amount of moisture in the air.

Cobalt nitrate, $\text{Co}(\text{NO}_3)_2$, is sometimes used in analytical work in testing for certain metals. It unites with certain metallic oxides, forming characteristically colored com-

pounds. Thus aluminum compounds, when converted into the oxide by heating with the blowpipe, give a blue coloration when further heated with cobalt nitrate solution.

Cobalt sulphide, CoS , black in color, is precipitated from alkaline solutions of cobalt salts by hydrogen sulphide. Like iron, cobalt forms two double cyanides with potassium, $\text{K}_4\text{Co}(\text{CN})_6$ and $\text{K}_3\text{Co}(\text{CN})_6$.

341. Nickel Ores and Extraction.—Nickel is nearly always a constituent of meteoric iron. The greater part of the nickel that the world uses comes from the province of Ontario in Canada, and from New Caledonia. The nickel compounds in the ores form only a small part of the whole. The Canadian ore is chiefly a sulphide of iron, containing about 2% each of nickel and copper. The treatment of the ore in its first steps resembles that used in the separation of copper from chalcopyrite. After the iron is removed by Bessemerizing, a matte rich in copper and nickel is obtained. This is roasted and the resulting oxides are reduced with charcoal. An alloy of copper and nickel is thus obtained. The two metals are separated by an electrolytic process.

342. Properties of Nickel.—Nickel is a hard metal, malleable, possessing a high melting-point, and resembling silver in color. It is capable of receiving and retaining a very high polish. Dry air does not attack it. Like cobalt, it dissolves readily in nitric acid, but is only slowly attacked by hydrochloric and sulphuric acids. Solutions of nickel salts have a beautiful, characteristic green color.

343. Uses of Nickel.—Nickel is of considerable practical importance because of its silver-white color and the fact that it does not readily tarnish in air. It is chiefly used

as a covering for other metals. It is deposited by an electrolytic process similar to that used in silver or copper plating. Nickel is a constituent of several important alloys. *Nickel steel*, which contains about 5% nickel, is both hard and tough; it is used in making armor-plates for battle ships. *Nickel coins* contain about one part nickel to three parts copper.

344. Compounds of Nickel. — The sulphate, NiSO_4 , and a double sulphate of nickel and ammonium are the salts used as electrolytes in nickel-plating. A compound of unusual character, known as nickel carbonyl, $\text{Ni}(\text{CO})_4$, is formed when carbon monoxide is kept in contact with nickel at a temperature of about 30° . In one method of separating nickel from copper, advantage is taken of this reaction.

Summary.

The principal *ores of iron* are the oxides, hematite and magnetite.

Cast iron is made by reducing the ore in a blast-furnace with coke as fuel; the earthy impurities pass into a slag.

Wrought iron is produced by burning out the carbon and impurities of cast iron in a reverberatory furnace.

Bessemer iron is made by blowing air through molten iron to remove carbon and impurities, and then adding spiegeleisen to furnish the desired percentage of carbon and manganese.

Steel is produced by melting together wrought iron and cast iron, or by dissolving carbon in wrought iron.

Iron forms *two series of compounds*. Ferrous compounds usually oxidize easily to ferric.

Ferric oxide is used as ore and as pigment.

Magnetic oxide is an ore. It is often produced artificially on iron by the action of steam, to protect the metal.

Iron-rust is a hydrated oxide resulting from the action of carbon dioxide and air on iron in the presence of moisture.

Ferric chloride is used in medicine.

Ferrous sulphate is used as a disinfectant, and as a reducing agent and in the production of paint.

Potassium ferrocyanide is used in the production of Prussian blue.

	CAST IRON.	STEEL.	WROUGHT IRON.
Carbon, per cent	4 to 7	0.8 to 2.8	Less than 0.25
Structure	Crystalline	Granular or fibrous	Fibrous
Melting-point	1200°	1400°	1600°
Specific gravity	7.2 to 7.5	About 7.7	7.8 to 7.9
Magnetic properties	Difficultly magnetized	Retains magnetism	Temporarily magnetized
Hardness	Hard	Hard (if tempered)	Soft
Elasticity	Elastic and brittle	Elastic and tenacious	Tenacious
Use	Casting and rigid structural purposes	Tools, springs	Blacksmith's iron, and wire

Bessemer iron resembles wrought iron in most of its properties, and is used for bars, rails, and structures.

Open hearth steel is used particularly for structures subject to vibrations.

Exercises.

1. What becomes of the ashes which would ordinarily result from the combustion of coke when the coke is burned in the blast-furnace?

2. Why is it necessary to produce a slag in the working of a blast-furnace? •

3. Why does the temperature of the converter rise when cold air is blown through it?

4. For what purposes is Bessemer iron and steel inferior to crucible steel? Why?

5. Why are not cast-iron pillars used in the upper stories of large buildings?

6. How is iron protected against corrosion?

7. Why was wrought iron probably the first form of iron worked by man?

8. Iron is one of the most abundant elements. Why does not iron occur to any extent in the free state?

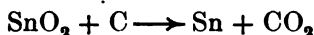
9. What kind of iron would you use for the manufacture of sheet iron? dynamo cores? nails? magnets? car wheels? steam radiators?

CHAPTER XXXII.

TIN AND LEAD.

Tin was one of the earliest metals known. The Phœnicians obtained it from the British Isles, which they called Cassiterides, land of tin. As a constituent of bronze it was used before iron.

345. Metallurgy of Tin.—Tin oxide, SnO_2 , is the only available ore. The present commercial supply comes from England, Germany, Australia, and the islands Billiton and Banca, near Sumatra. Tin oxide is reduced by heating it in a reverberatory furnace with coal:



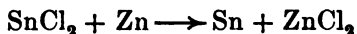
The molten metal which collects at the bottom of the furnace is drawn off and cast into ingots, known commercially as *block tin*. It is purified by heating it on the inclined hearth of a furnace. The less easily melted impurities remain, while the easily melted tin flows down the hearth. It is further purified by being poled, in the same way as blister copper.

346. Properties of Tin.—Tin is a white, lustrous metal, capable of withstanding the ordinary atmospheric agents. Being soft and malleable, it can be cut and hammered. Like zinc, it is crystalline in structure, and if a bar of tin is bent, it makes a peculiar noise (tin cry), probably caused by the friction of the crystals. Like zinc, its

physical properties vary considerably with the temperature. It melts at a rather low temperature, and burns, forming a white oxide.

With acids tin does not react like any *one* of the other metals; with hot, concentrated hydrochloric acid, it forms *stannous chloride*, SnCl_2 ; with sulphuric acid it reacts like copper; nitric acid oxidizes it to a white, insoluble solid known as metastannic acid.

Tin can be separated from solutions of its compounds as a gray, spongy mass, by immersing a strip of zinc in the solution :



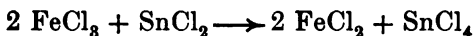
347. Uses of Tin.—The resistance of tin to ordinary corrosive agents is utilized in protecting other metals by covering them with a layer of tin. Ordinary *tinware* is sheet iron, which has been thoroughly cleaned and dipped into melted tin. Copper vessels and brass pins are similarly treated.

Tin foil is tin, hammered or rolled into thin sheets; cheaper grades contain some lead. Tin pipes are used to convey soda water and beer from the tanks to the faucet.

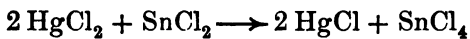
Many common alloys contain tin. Bronze contains copper, tin, and often zinc. The one cent piece is bronze. Pewter and solder contain tin and lead. Britannia metal and white metal contain varying proportions of tin, antimony, and copper. Anti-friction and fusible metals often contain considerable tin.

348. Compounds of Tin.—*Stannous chloride*, formed by the reaction of tin and hydrochloric acid, is the only common compound. The hydrated salt, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is technically known as *tin crystals*, and is extensively used in

mordanting. It produces more brilliant shades than the aluminum compounds. Stannous chloride is a strong reducing agent in acid or in alkaline solutions. Ferric salts are reduced by it to ferrous compounds :



Mercuric compounds are first reduced to mercurous salts, and with an excess of the reagent, to metallic mercury :



The *stannic chloride*, SnCl_4 , is a colorless, fuming liquid, which is readily decomposed by water.

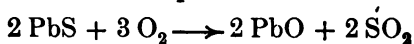
Thus the valence of tin may be two or four, as shown by the existence of stannous and stannic compounds. *Stannous sulphide*, SnS , is a brown, insoluble compound. *Stannic sulphide*, SnS_2 , is a yellow, insoluble solid used as a pigment.

LEAD.

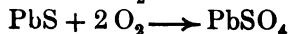
Owing to the wide distribution of its compounds and the ease of separation from its ores, lead has been used by man from the earliest times.

349. Metallurgy. — The most common ore is the sulphide, galena, PbS , large deposits of which are found in Missouri, Illinois, and Colorado. The method employed in the extraction depends largely upon the purity of the ore.

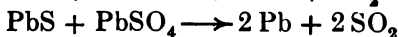
Ores having a large percentage of lead are roasted in a reverberatory furnace (Fig. 118) until *part* of the sulphide has been oxidized, forming lead oxide, sulphur dioxide, and some lead sulphate :



and



When the oxidation has proceeded far enough, the air is shut off by closing the doors, and the mixture is heated to a higher temperature. The remaining lead sulphide now reacts with the lead oxide and sulphate, forming lead and sulphur dioxide :



The lead is moulded into ingots known as *pig lead*. When there is a considerable amount of precious metal in the lead, it is known as *base bullion*. The working of this has been described under silver (§ 293, Parkes' process).

Ores poor in lead are reduced in a blast-furnace similar to that used for copper; indeed, they may be separated from the ore at the same operation,

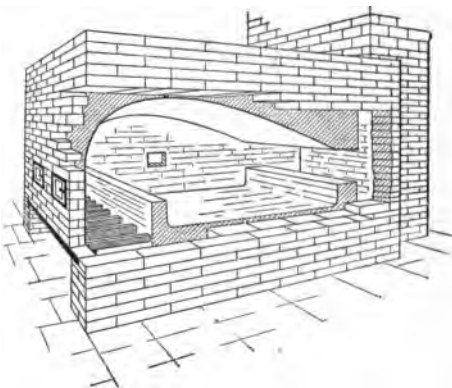


Fig. 118. Reverberatory Furnace.

the heavy lead settling beneath the matte and slag.

Electrolytic reduction of galena is effected in a bath of dilute sulphuric acid. The crushed galena is made the cathode, the bottom of the pan the anode. The lead is obtained as a spongy mass. The hydrogen sulphide produced is conducted away to a combustion chamber and converted into sulphuric acid or sulphur.

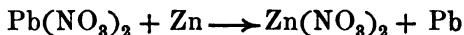
350. Properties of Lead. — Lead is a soft, bluish white metal. The brilliant lustre, apparent when freshly cut,

soon disappears, owing to the formation of a thin film of oxide. This coating, however, protects it from further change. Lead is not very tenacious, but being soft it can be rolled into sheets or forced through a die to form pipe.

When heated in air, lead oxidizes. Cold hydrochloric or sulphuric acid have very little effect on it. Nitric acid, acetic acid (from vinegar) and many vegetable acids dissolve it, forming soluble salts. Water containing carbon dioxide corrodes lead, hence the objection to lead water-pipes which would be affected by such water.

All lead compounds are poisonous, and if taken into the system cause serious illness. Even minute quantities in the water will ultimately produce this result, for lead compounds are excreted with difficulty, and therefore accumulate in the body. Painter's colic is a form of chronic lead-poisoning.

On immersing a strip of zinc in a solution of lead salt, the lead separates in a characteristic crystalline deposit, the *lead-tree*:



The formation of insoluble chrome yellow by addition of potassium dichromate to a solution of a lead salt is another characteristic property of lead salts:



351. Uses of Lead. — Lead is very extensively used for pipes and as a sheathing for cables, as it is easily cut, bent, or soldered. Lead pipe is now made by forcing the hot lead through a die by a piston. The opening of the die is partly obstructed by a solid cylindrical rod attached to the upper surface of the piston. The rod moves upward

with the piston, and the pipe is formed by the lead being squeezed out between the rod and the wall of the die.

Sheet lead was formerly used for roof covering much more than at present. It is very widely used as a lining for tanks, cisterns, and cells used in electrolytic operations. The Chinese have long used it for lining tea-chests.

Thin sheet lead, alloyed with tin, is often used instead of pure tin-foil. *Type metal* contains lead with tin and antimony, which harden it and form an alloy that expands in solidifying. Thus it fills the moulds and makes a clear-cut type. *Solder* and fusible metals are largely lead and tin. Such alloys are forced through a die in the same manner as lead pipe, forming a wire used as *fuse wire*.

Large quantities of lead are used in the manufacture of *shot*. As already stated, the shot contains a small amount of arsenic. The molten metal is run into a perforated vessel, and falls in streams a long distance into the water. In falling, the streams separate into drops which solidify before they reach the water. The sizes of shot are assorted by allowing them to run down inclined planes or screens of different meshes. The smallest shot fall through the nearest (smallest) openings into the bins, the larger shot going on to the larger holes. Irregular shaped pieces will not roll well, and are finally pushed off at the end. The shot are polished by tumbling them in a barrel or drum with a little graphite.

COMPOUNDS OF LEAD.

352. Oxides. — *Lead oxide*, PbO , is known as massicot when of a yellowish tint; when it solidifies from the molten state it is buff-colored and crystalline, and is known as *litharge*. The presence of bismuth sometimes gives the

litharge a yellowish color. Litharge is made by heating lead in the air. Considerable quantities are produced in the cupellation of silver. It is largely used in the preparation of oils and varnishes, of glass and glazes, and of other compounds of lead. A mixture of litharge and glycerine is used as a cement, especially for stone and glass.

Red lead, or minium, is a bright red powder, known as American vermilion. It is prepared by heating lead or lead oxide in the air, oxygen being absorbed in the operation. The tint and composition often vary with the manipulation. Its composition may be represented by the formula: Pb_3O_4 or $(2 PbO \cdot PbO_2)$. It is used in making flint glass and as a pigment, especially on ironwork. Being an oxidizing agent, it hastens the hardening of the oils used in paint. On this account a mixture of red lead and oil is used by plumbers and gas-fitters to make tight joints.

Lead dioxide, PbO_2 , is a brown powder obtained by treating red lead with nitric acid. It is used as an oxidizing agent on the negative plates of storage batteries.

353. White Lead. — *Basic lead carbonate*, white lead, is a heavy, white, opaque powder. It mixes well with linseed oil and forms a valuable paint base. The body of many paints is white lead, which furnishes opacity or *body*, the tint being furnished by admixed color. Owing to the importance of white lead, many methods have been devised for its production.

The *Dutch process of corrosion* has been in use three hundred years, and although details have been improved, remains essentially the same. Ridged and perforated disks, or "buckles," of lead (Fig. 119) are piled on a shelf in a loosely covered earthenware pot, the lower part of which contains a little dilute acetic acid. Such pots are placed

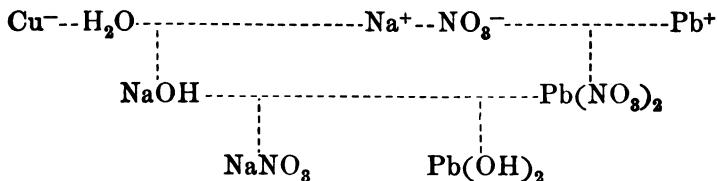
side by side and covered with tan-bark; other layers of pots are added to a considerable height. The decaying mass generates heat and carbon dioxide. The acetic acid is volatilized, forming basic lead acetate. The carbon dioxide resulting from the fermentation changes this to the basic carbonate. Three or four months are required for the complete



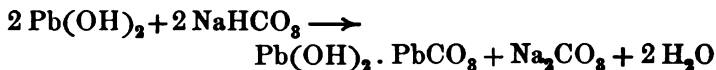
Fig. 119.

corrosion of the lead; the right-hand portion of Fig. 119 represents a jar broken open to show the lead buckles after corrosion. The white lead is removed from the jars, washed, ground, and sifted. Small pieces of unaltered lead are removed by the sifting. The white lead is then ground in oil and is ready for use. The corrosion process requires much time but yields good paint.

In a recent *electrolytic process* a copper cathode and a lead anode are placed in a solution of sodium nitrate. The electrolyte furnishes sodium hydroxide at the cathode and nitric acid at the anode. The nitric acid reacts with the lead, forming lead nitrate. This lead nitrate reacts with the sodium hydroxide, again forming sodium nitrate and an insoluble lead hydroxide which settles out, so that the process is continuous, only the lead needing renewal:



The lead hydroxide is treated with sodium bicarbonate, forming white lead of a different composition from that made by the Dutch process.



The process is rapid and is said to give a paint of good covering power.

The Dutch process aims at a white lead with the composition $2 \text{Pb(OH)}_2 \cdot \text{PbCO}_3$, but the composition of its product varies.

354. Chrome Yellow. — *Lead chromate*, PbCrO_4 , is an insoluble, bright yellow powder, prepared by mixing solutions of lead salts and chromates. It is used in dyeing and painting.

Summary.

The chief ore of *tin* is the oxide, which is reduced by heating with coal.

Tin is soft, malleable, and crystalline. Its specific gravity is 7.3, and it melts at 232°C .

It is unaltered by air at ordinary temperatures.

Tin is used as foil and as a coating for iron. It is a constituent of bronze, pewter, and white metal.

Stannous chloride is formed by the action of hydrochloric acid on tin. It is a reducing agent.

Lead occurs chiefly as a sulphide. The ore is reduced in a reverberatory furnace, or by electrolysis.

Lead is soft, malleable, and tenacious. Its specific gravity is about 11.3 and its melting-point 327°C .

It oxidizes in air and dissolves in nitric and acetic acids. Water containing carbon dioxide corrodes it, producing poisonous compounds.

Lead is used for pipe, as a lining and covering material, in type-metal, solder, and shot.

Lead oxides are made by heating lead in air. They are used in making varnishes and glass, and as pigments. Lead dioxide is used in storage batteries.

White lead is basic lead carbonate and chrome yellow is lead chromate.

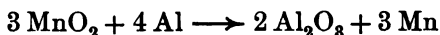
Exercises.

1. Which forms a better protective coating for iron, tin or zinc?
2. State the relative advantages of lead and tin-plate as a coating for roofs.
3. Why were lead and tin early obtained in the metallic state?
4. Why is tin-foil superior to lead-foil for wrapping articles of food?
5. Why is arsenic put in shot?
6. What is litharge? red lead? white lead?
7. Why is red lead called a drier in paints and varnishes?
8. What advantage has zinc-white over white lead as a paint base? white lead over zinc-white?
9. What are the characteristic properties of glass containing lead?
10. How much lead can be extracted from a ton of galena?

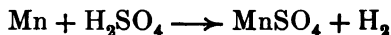
CHAPTER XXXIII.

MANGANESE AND CHROMIUM.

355. Preparation and Properties of Manganese. — The most important ore of manganese is pyrolusite, which is crude manganese dioxide. The metal is obtained by igniting a mixture of pyrolusite and aluminum powder. Heat is applied at one point and the action spreads through the whole mass :



Manganese is a hard metal resembling steel in appearance. It oxidizes in moist air and, when finely divided, decomposes boiling water. It dissolves readily in sulphuric and hydrochloric acids, with the liberation of hydrogen and the formation of the corresponding salt of the manganous ion, Mn^{++} :



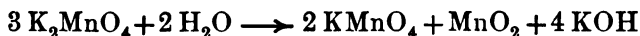
Its alloys, ferro-manganese and spiegeleisen, are used in the production of Bessemer iron and steel.

356. Manganese Compounds. — Manganese forms several oxides, of which the most important is the *dioxide*, MnO_2 . This is a hard, black solid which conducts electricity. It is a powerful oxidizing agent, as we have already seen in the preparation of chlorine from hydrochloric acid (§ 54). Its conducting power and oxidizing action make it a valuable depolarizer in voltaic cells.

The manganous salts are stable compounds, whose water solutions are pink. The salts of the manganic ion Mn^{+++} are unstable.

357. Manganates and Permanganates. — In addition to the salts in which manganese occurs as a positive ion, there are others in which it is a constituent of a negative ion. The most important of these salts are the manganates and the permanganates, both of which contain the radical MnO_4 . In the manganates the ion is bivalent, MnO_4^{--} ; in the permanganates it carries only one charge, MnO_4^- . Corresponding to this difference in valence of the ion are differences in the properties of the salts. This can best be shown by comparing potassium manganate and potassium permanganate.

Potassium manganate is made by fusing a manganese compound with potassium hydroxide in the presence of air or an oxidizing agent, dissolving the residue and evaporating the solution in a vacuum. The crystals obtained are dark green. They are decomposed by water, with the liberation of manganese dioxide and the formation of potassium permanganate, KMnO_4 .



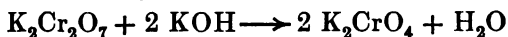
Potassium permanganate is obtained as dark purple crystals, which dissolve in water, yielding a violet solution. It is a powerful oxidizing agent.

358. Chromium. — Chromium occurs chiefly as chromite, $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$. From this it is reduced by aluminum in a manner analogous to that employed in the preparation of manganese. It is a hard, steel-gray metal, unaltered by the air. When very small quantities are added to steel, the tenacity and hardness are increased.

359. Oxides of Chromium. — The two important oxides of chromium are *chromic oxide*, Cr_2O_3 , and *chromic anhydride*, CrO_3 . The chromic salts are derived from chromic oxide; the most important is the double sulphate of potassium and chromium, $\text{K}_2\text{Cr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, known as chrome alum. A solution of chromic anhydride yields CrO_4^{--} ions, but the acid is isolated with difficulty, as it breaks up into chromic anhydride and water. The solution of the anhydride is a powerful oxidizing agent, and its derivatives, the chromates and dichromates, resemble it in this respect.

360. Chromates and Dichromates. — *Potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, is the basis of most of the chromium salts. It is prepared by heating chromite with potassium carbonate and lime in a reverberatory furnace. It forms large red crystals from solution or fusion; these are somewhat soluble in cold water, and their solubility increases rapidly as the temperature rises. Potassium dichromate reacts with sulphuric acid, with the formation of chromium sulphate and the liberation of oxygen. This oxidizing action is frequently made use of in depolarizing voltaic cells. Sodium dichromate is very similar to potassium dichromate, but has the added advantage of being more soluble. Most of the dichromates are red in solution.

Potassium chromate, K_2CrO_4 , is prepared by the addition of potassium hydrate to the dichromate:



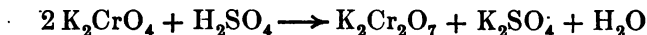
It forms yellow crystals, more soluble than those of the dichromate. The relation between the chromate and the dichromate may be seen if the formula of potassium dichromate is written $\text{K}_2\text{CrO}_4 \cdot \text{CrO}_3$. Other complex chromates are known containing more than one CrO_3 group.

Lead chromate, PbCrO_4 , made by treating a soluble lead salt with a chromate or dichromate, is a yellow, insoluble compound, known as chrome yellow, and used as a pigment.

361. Relations of Chromium Compounds. — When chromous compounds (*e.g.* chromous chloride, CrCl_2) are converted into chromic compounds (*e.g.* chromic chloride, CrCl_3), the valence of chromium changes from *two* to *three*. If a chromic compound is fused with sodium bicarbonate and some oxidizing agent, such as potassium chlorate, a chromate is obtained.

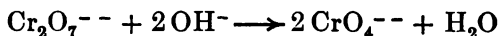
The valence of chromium in the chromates is six. The changing of chromous into chromic compounds, and the changing of the latter into chromates, are cases of oxidation.

In the presence of acids, even weak ones, the soluble chromates are converted into dichromates.



As the valence of chromium in each case can be shown to be six, it appears unadvisable to consider this as a case of oxidation. Here the hydrogen ion of the acid seems to be the active agent.

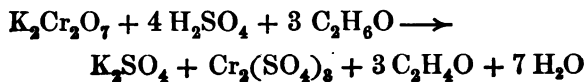
In the presence of an excess of hydroxyl ions, that is, in alkaline solutions, the soluble dichromates are changed to chromates.



This change should not be considered as a case of reduction.

When alcohol or some similar substance is added to a mixture of sulphuric acid and potassium dichromate, the change in color from orange to green shows that the

chromium has been changed from a dichromate to a chromic compound. The valence of chromium has been reduced from six to three. This is a case of reduction.



CHAPTER XXXIV.

THE PERIODIC LAW.

362. Early Attempts at Classification.—The discovery of new elements and the investigation of their properties led the earlier chemists to recognize the existence of certain families or groups of elements. In 1829 Döbereiner called attention to certain *triads* or groups of three elements in which the atomic weight of the second element was the arithmetical mean of the first and third. He also pointed out that the properties of the middle element were intermediate between those of the other two. This was the first attempt to show that a relation existed between the properties of elements and their atomic weights. The elements chlorine, bromine, and iodine form a well-marked triad :

$$\frac{35.5 + 127}{2} = 81.2;$$

the atomic weight of bromine, 80, approximates the mean, 81.2.

Other attempts to classify the elements were made from time to time, but it was not until 1860–1870 that any system received recognition. In 1863–1864, Newlands, an Englishman, directed attention to the fact that the elements showed surprising regularity when arranged in order of their atomic weight. He said the properties of each element seemed to be repeated in a measure by those of

the eighth element following it. This relation is called the *law of octaves*. Newlands' system of classification, although it contained many of the principles we use to-day, attracted little notice. Lacking a strong advocate to push its claim, the new system was soon forgotten. In 1869 Mendelejeff, a Russian chemist, aroused great interest in scientific circles by bringing forward a system of classification which for the first time brought all the elements into a comprehensive scheme of relationship based upon their atomic weights. A few months later, Lothar Meyer, a German, put forward a similar system which he had worked out independent of Mendelejeff. Although Meyer has done much to assist in classifying the elements, it is now generally acknowledged that Mendelejeff is entitled to the greater credit, and the system we use to-day bears the name of the Russian chemist. It was Mendelejeff who brought forward a system which he elaborated and successfully defended against the many attacks made upon it.

363. Periodic Law. — Beginning with lithium, let us arrange the elements in the order of their atomic weights:

LITHIUM.	GLUCINIUM.	BORON.	CARBON.	NITROGEN.	OXYGEN.	FLUORINE.
7	9	11	12	14	16	19

Lithium is an element with strong metallic or basic properties; glucinum, Be, is less metallic; boron has some metallic properties, but generally acts like a non-metal; carbon forms weak acids; nitrogen shows stronger acid properties; oxygen is characteristically acid; fluorine, at the end, is the most pronounced acid element. Hence, the seven elements show a gradation in properties from a pronounced metal to an element of strongly acid charac-

ter. A similar transition can be shown for other properties as we pass from lithium to fluorine. Thus the properties seem to vary with the atomic weights, or, in mathematical language, the properties are functions of the atomic weights. Sodium, the eighth element after lithium, closely resembles it, and may be placed directly beneath as the beginning of another horizontal row:

Lithium	Glucium	Boron	Carbon	Nitrogen	Oxygen	Fluorine
7	9	11	12	14	16	19
Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulphur	Chlorine
23	24	27	28	31	32	35.5

Magnesium repeats the properties of glucium, and the characteristics of boron recur in aluminum. That is, the eighth element repeats the properties of the one taken as the first. Silicon, then, should be like carbon, and phosphorus should resemble nitrogen. These we know to be facts. Since the properties recur or are repeated at regular intervals, the properties are said to be periodic; or, as Mendelejeff expressed it, "a periodic repetition of properties is obtained if all the elements be arranged in the order of the atomic weights."

364. Long and Short Periods. — The table on page 368 is arranged according to the principle of classification just given. Omitting for the present the first vertical column marked Series O, the seven elements, from lithium to fluorine, form a horizontal series known as a *short period*. The set of elements from sodium to chlorine make the second short period. Beginning in the next line with potassium, it is found that the metallic properties do not disappear so rapidly as in the first and second short periods. Manganese, the seventh element, has some well-

PERIODIC CLASSIFICATION OF THE ELEMENTS.

	SERIES 0.	SERIES I.	SERIES II.	SERIES III.	SERIES IV.	SERIES V.	SERIES VI.	SERIES VII.	SERIES VIII.
	R	RO ROH	RO ROH ₂	RO ₂ ROH ₃	RO ₂ ROH ₄	RO ₂ RO ₃ H ₅	RO ₂ RO ₃ H ₅	RO ₂ RO ₃ H ₅	RO ₂ ← Oxide ← Hydroxide
1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	
2	Ne 20	Na 23	Mg 24.3	Al 27	Si 28.4	P 31	S 32	Cl 35.5	
3	A 39.9	K 39	Ca 40	Sc 44	Ti 48.1	V 51	Cr 52	Mn 55	Fe Co Ni 56 59 58.7 Cu 63.6
4	—	(Cu) (63.6)	Zn 65.4	Ga 70	Ge 72.5	As 75	Se 79.2	Br 80	
5	Kr 81.8	Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96	—	Ru Rh Pd Ag 101.7 103 106.5 108
6	—	(Ag) (108)	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.6	I 127	
7	X 128	Cs 133	Ba 137.4	La 139	Ce 140	—	—	—	
8	—	—	—	—	—	—	—	—	
9	—	—	Yb 173	Tl 204	—	Ta 183	W 184	—	Os Ir Pt Au 191 193 195 197
10	—	(Au) (197)	Hg 200	—	Pb 207	Bi 208	—	—	
11	—	—	Ra ? 225	—	Th 232	—	U 238	—	

marked metallic properties. Iron is not placed under potassium, but is put in an eighth series together with cobalt and nickel. There is a gradual increase in the metallic properties as we pass through these three elements to the more metallic copper. The elements from copper to bromine show a gradual decline in the metallic properties and an increase in the acid properties until the strongly acid element bromine is reached. Hence we have a series of seventeen elements, beginning with potassium and ending with bromine. This is known as a *long period*. The elements from rubidium to iodine constitute the second long period. In this period the elements of the eighth series, ruthenium, rhodium, and palladium, form a bridge in the transition of properties from the seventh series to the first.

365. Families or Groups of Elements.—It is evident from the periodic nature of the classification that all the elements in one of the vertical series have certain resemblances. The relationship, however, is much closer in some cases than in others. Thus, in Series II, calcium, strontium, and barium are more closely allied to each other than they are to magnesium, zinc, cadmium, and mercury. These last four elements form a closely related group. That is, the more closely related elements are not successive, but alternate in a vertical series. The result of this alternate arrangement is to divide each vertical series into two families or groups. In Series VI, chromium and molybdenum are in one family, while sulphur, selenium, and tellurium form the other. The halogen elements, chlorine, bromine, and iodine, in Series VII, afford one of the best examples of a closely related group. Lithium, potassium, rubidium, and caesium, in

Series I, are a group of soft, waxy metals of high lustre and low boiling-points. They decompose water readily, forming caustic bases. A study of their properties shows that a gradual transition in properties accompanies the increase in atomic weights.

A similar variation in properties in accordance with the increase in atomic weight in a vertical series is well brought out in the study of the elements of the halogen group. At the head of each vertical series are placed some general formulas for the oxides and hydroxides of the elements in the series beneath. R is the general symbol for an atom of the element under consideration. Thus in Series I the general formula of the oxide is R_2O , and we have the oxides Li_2O , Na_2O , K_2O , Cu_2O , and so on.

These general formulas may be extended to include other compounds, as the chloride, nitrate, and sulphate:

SERIES I.			SERIES II.	
	FORMULA.	ILLUSTRATION.	FORMULA.	ILLUSTRATION.
Oxide	R_2O	K_2O	R_2O_2 (= 2 RO)	CaO
Hydroxide	ROH	KOH	$R(OH)_2$	$Mg(OH)_2$
Chloride	RCl	KCl	RCl_2	$HgCl_2$
Nitrate	RNO_3	KNO_3	$R(NO_3)_2$	$Zn(NO_3)_2$
Sulphate	R_2SO_4	K_2SO_4	RSO_4	$BaSO_4$

SERIES III.		
	FORMULA.	ILLUSTRATION.
Oxide	R_2O_3	Al_2O_3
Hydroxide	$R(OH)_3$	$Al(OH)_3$
Chloride	RCl_3	$AlCl_3$
Nitrate	$R(NO_3)_3$	$Al(NO_3)_3$
Sulphate	$R_2(SO_4)_3$	$Al_2(SO_4)_3$

It can be seen from the study of these general formulas that there is a regular increase in valence as we proceed from the first series to the seventh.

366. Position of the Inert Gases and of Hydrogen.— With the discovery of argon and other inert gases, considerable discussion arose as to their proper place in the periodic system. Since no compounds of these elements are known, they cannot be properly placed in any one of the vertical series. Accordingly it has been deemed best to form a separate vertical series for these elements at the beginning of the classification, and mark it Series O.

It will be noticed that hydrogen is not placed in the table given on page 368. Since it has the smallest atomic weight, its natural position would be the beginning of the classification. If, however, it were placed in Series O, it would be classed with the inert elements from which it differs decidedly in its properties. A similar difficulty would arise if hydrogen was placed in Series I, which contains the alkali metals. At present the position of hydrogen is so uncertain that it is left out of many periodic tables.

367. Significance of Vacant Spaces in Table.— It will be noticed that the series of elements is almost complete until the atomic weight of 145 is reached, while among the elements of a greater atomic weight many vacancies exist. Considerable speculation has arisen as to the meaning of these gaps. Perhaps in time other elements will be discovered to fill in these blanks.

368. Value of the Periodic System.— *Mendelejeff's system has been of great value in predicting the discovery of new elements.* In fact, in the years immediately following the

announcement of the law, when its validity was so questioned, the fulfilment of Mendelejeff's predictions as to the existence and properties of elements then unknown, gave striking evidence of the correctness of the new system of classification. The table following shows the predictions and their verification in the case of an element which Mendelejeff called *eka-aluminum*, and which is now known as gallium:

PROPERTIES.	PREDICTED.	DISCOVERED.
Atomic weight	About 69	69.9
Melting-point	Low	30.1°
Specific gravity	About 5.9	5.93
Action of air	None	Slightly oxidized at red heat
Action on water	Decomposes at red heat	Decomposes at high temperatures

The predictions by Mendelejeff and their subsequent verification were equally striking in the cases of eka-boron (scandium) and eka-silicon (germanium).

The second use of the classification is in the adjustment and revision of atomic weights. In the early days of the classification many of the elements were improperly placed. It was suggested that this might be due to incorrect values for the atomic weights. This led to more accurate determinations of the atomic weights. In many cases results were obtained which admitted of the elements being placed in the table according to their proper relationships. Chemical research has been greatly stimulated by these revisions of atomic weights.

The development of a systematic study of the elements has been the greatest service of the periodic law. A knowledge

of relationships has simplified the determination of the physical and chemical properties not only of the elements but of their compounds. Although the system of Mendelejeff is not perfect, and no exact numerical relations have been found, the periodic classification is of great aid to the student of descriptive chemistry.

CHAPTER XXXV.

COMPOUNDS OF CARBON.

369. Most of the elements we have studied form comparatively few and simple compounds, which are generally ionized in solution. Carbon, on the other hand, forms many compounds, often of complex structure and not readily ionized. As many of these compounds are formed in vital processes, the study of such materials was known as *organic chemistry*. The term as now used means the study of carbon compounds.

370. Sources. — Practically, carbon compounds are not made from carbon, as carbon reacts indifferently with reagents. Certain easily obtainable compounds of carbon which react more readily are used for the preparation of others. A few compounds, as sugar, quinine, starch, and turpentine, are obtained directly from plants. Many fats, oils, and waxes, are obtained from plants and animals. Many other compounds are obtained from the distillation of petroleum and from the destructive distillation of wood, coal, and bones. By such destructive distillation, compounds are obtained which were formed during the heating and which did not exist in the original material.

371. Destructive Distillation of Wood. — When wood is heated without access of air, volatile materials pass off and charcoal remains. As these volatile materials contain several valuable substances, the operation is carried out

on a large scale. Wood is heated in cylindrical iron retorts (Fig. 120, *a*). The volatile materials are cooled, and while a portion remains gaseous and is used as fuel, a large part is condensed (Fig. 120, *b*) to a dark, tarry liquid.

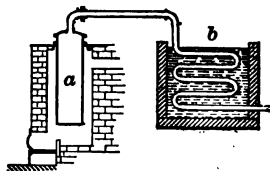


Fig. 120.

The tarry mass is distilled with slaked lime at a low temperature, and wood alcohol is obtained. The object of adding the lime is to neutralize acid present in the mass. The acids, principally acetic acid, are recovered from the residue by the usual method, distillation with sulphuric acid.

When bone is heated, it undergoes changes analogous to those of wood. Gas, volatile liquids, and boneblack are obtained. The liquid *bone-oil* is a valuable source of carbon-nitrogen compounds.

372. Destructive Distillation of Soft Coal. — When soft coal is distilled in the preparation of coal-gas (page 180, Fig. 56), four products are obtained, — coal-gas, ammonia, coal-tar, and coke. The coal is heated in horizontal pipes called *retorts*, and the volatile materials expelled. The non-volatile residue is coke, principally carbon and the ash constituents. The gaseous materials are cooled in pipes where tarry materials condense and are collected. The gases then pass to the *scrubber*, where they come in contact with water dripping over wooden lattice work. Here the ammonia is dissolved in the water, and more tar separates. The working of the ammoniacal liquid has been described in the chapter on ammonia (§ 163). The gas is freed from sulphur compounds by passing through boxes containing slaked lime or iron oxide, and then passes to the

holders for distribution. Various compounds are obtained from the tar by fractional distillation. Benzene, carbolic acid, and naphthalene are some products from coal-tar; they are invaluable in the preparation of many pharmaceutical materials and dyestuffs.

373. Petroleum and its Distillation. — Petroleum is a dark, oily liquid occurring in the earth. It is believed to be due to changes brought about in organic matter under the influence of heat and pressure, as in the case of coal, or, perhaps, by the reaction between water and metallic carbides at great depths below the surface of the earth. Petroleum is a mixture of many carbon-hydrogen compounds. Practically no *pure* compounds are separated from it, but the many commercial articles prepared from petroleum are mixtures obtained in its distillation.

The crude petroleum is distilled in iron retorts (Fig. 121) connected with condensers and receiving-tanks. As the petroleum is a mixture, the lighter substances with

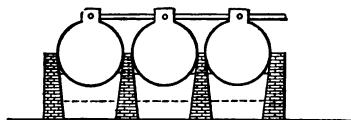


Fig. 121.

lower boiling-points are first volatilized, and the temperature gradually rises until only a pitchy mass remains in the retort. A hydrometer indicates the specific gravity

of the liquid as it runs from the condenser, and, as the density of the distillate varies, it is run to appropriate tanks.

Gasolene, naphtha, benzine, and kerosene are some of the trade names of the fractions into which the separation is made. They differ in density, volatility, and kindling temperature, each being a mixture of several compounds.

As in the case of kerosene, a further purification is

often needed. To rid the kerosene of materials which would not burn well or might smell, the liquid is agitated successively with concentrated sulphuric acid, sodium carbonate solution, and water. The light petroleum products are used almost entirely for solvents and fuel. The residue in the still, after the removal of the lighter oils, is further distilled at a higher temperature in another retort, and heavier materials obtained, such as the various grades of lubricating oils, vaseline, and paraffin. The mineral oils have largely displaced animal and vegetable oils as lubricants. The paraffin is used in candles, as a preservative coating, in waterproofing, and for many other purposes. The final residue in the retort is coke, and is used in the manufacture of electric-light carbons or for fuel.

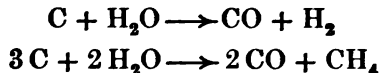
Natural gas is a mixture of combustible gases issuing from the earth in many localities, often under considerable pressure. When petroleum is brought to the surface and distilled, considerable gaseous material is separated. The chief constituent of these natural gases is methane. Where natural gas is obtained in quantity, it is, of course, a valuable fuel.

HYDROCARBONS.

There are many compounds of carbon with hydrogen; these are called hydrocarbons.

374. Methane, or Marsh-gas.—Methane, CH_4 , is a colorless, odorless gas which, when pure, burns with a non-luminous flame. It is often formed in the decomposition of organic matter, as in swamps, hence its common name, *marsh-gas*. It is the principal constituent of natural gas. In soft-coal mines, the miners call it *fire-damp*, as its mixture with air is a serious source of danger.

It is formed in the production of water-gas when the temperature of the furnace is low :



Other than fuel it is of no practical importance, as it reacts with very few materials.

375. Paraffin Series. — Methane is the simplest member of a *series* of hydrocarbons, all of which resemble it in their lack of chemical activity, whence the name *paraffin series*.

PARAFFIN SERIES.

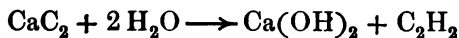
	FORMULA.	MOLECULAR WEIGHT.	BOILING-POINT.	FREEZING-(OR MELTING-)POINT.	
Methane	CH_4	16	-164°C	—	} Ordinarily gaseous
Ethane	C_2H_6	30	-89.5	—	
Propane	C_3H_8	44	-38	—	
Butane	C_4H_{10}	58	$+1$	—	
Pentane	C_5H_{12}	72	36	—	} Liquid
Hexane	C_6H_{14}	86	71	—	
Hexadecane	$\text{C}_{16}\text{H}_{34}$	226	288	18°	} Solid
Octadecane	$\text{C}_{18}\text{H}_{38}$	254	317	28	

It will be observed that the formula of each member differs from the preceding by CH_2 ; such a series is called a homologous series. The general formula for the series is $\text{C}_n\text{H}_{2n+2}$. With increasing molecular weight there will be noticed a rising of the boiling-point and the tendency to assume the solid form in the higher members. It is mixtures of these compounds that occur in petroleum products.

376. Benzene. — Benzene, or benzol, C_6H_6 , is a light, colorless, volatile liquid, having a peculiar odor. It is ob-

tained from that portion of coal-tar that boils at 80°–85°. Benzene burns with a smoky flame. It is a good solvent for resins and fats. Its principal use, however, is for the production of more complex compounds. Unlike the paraffin hydrocarbons, the coal hydrocarbons react with comparative ease, as with nitric and sulphuric acid, forming important compounds used in the preparation of dyestuffs. Benzene is the first member of a series, C_nH_{2n-6} , analogous to the paraffin series.

377. Acetylene. — Acetylene has been mentioned as resulting from the reaction of calcium carbide and water :

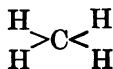


It has a peculiar, disagreeable odor, noticeable when a Bunsen burner is lighted at the base. It is here formed by the incomplete combustion of the gas. Ordinarily it burns with a smoky flame, but with a suitable burner it furnishes a brilliant light which nearly approaches sunlight in *color*. Acetylene is exploded by concussion or by an electric spark, so that it is not often made in quantity, but is made as used. Its chief use is as an illuminant.

SUBSTITUTION PRODUCTS.

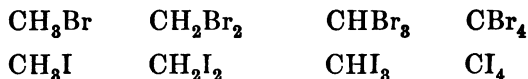
378. Relation to Methane. — The numerous compounds of carbon may appear puzzling, but a general view of them is simplified if we regard them as *substitution* products of methane.

If we consider any hydrogen atom of methane, CH_4 , it is combined with a carbon atom and three other hydrogen atoms :



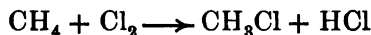
The group (CH_3) has evidently combining power equal to one hydrogen atom, so that we may say its valence is one. Now, we can conceive of one hydrogen atom in a molecule of methane replaced by its equivalent (CH_3) so that a compound $(\text{CH}_3)(\text{CH}_3)$ would result, having the composition of ethane, C_2H_6 . In a similar manner, if one atom of hydrogen in ethane is replaced by its equivalent, CH_3 , we would have C_3H_8 for the third member of the series, and so on.

Chlorine is equivalent to hydrogen in valence (HCl). If one atom of chlorine was substituted for one of the hydrogen atoms of methane, we would have CH_3Cl ; if two were substituted, CH_2Cl_2 ; similarly, CHCl_3 and CCl_4 . In like manner we could have :



All of these compounds are known, but it should be remembered that while the structure of such compounds is *explained* on the supposition of substitution, they are usually *not made* that way.

379. Monochlormethane. — Monochlormethane, *methyl chloride*, CH_3Cl , is a colorless gas having an ethereal odor. Methane and chlorine react :



The reaction is too violent to be of practical use. The chloride is commercially prepared from a by-product obtained in sugar-refining. Methyl chloride is easily liquefied, and the liquid is used as a local anesthetic, producing insensibility by freezing. It has also been used in ice machines.

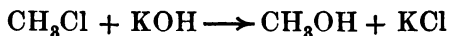
380. Chloroform and Iodoform. — Trichlormethane, *chloroform*, CHCl_3 , is a heavy, colorless, easily flowing liquid. It has a peculiar odor and a sweet taste. It is scarcely soluble in water. Chloroform is a most valuable anesthetic and an important solvent. It is prepared by distilling alcohol or acetone with a solution of bleaching-powder.

Tri-iodomethane, *iodoform*, CHI_3 , is a light yellow powder with a characteristic odor. It is useful as an antiseptic. Iodoform may be prepared by the reaction of iodine and alcohol rendered slightly alkaline.

ALCOHOLS.

Alcohols, as a general name, is applied to a class of bodies resembling methyl and ethyl alcohols. They may be briefly described as hydroxyl substitution products of hydrocarbons.

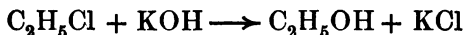
381. Methyl or Wood Alcohol. — The hydrogen in hydrocarbons can be substituted by other elements or groups. This substitution often has to be accomplished by an indirect process. For example, if monochlormethane is heated with dilute potassium hydroxide, the following reaction takes place :



The compound CH_3OH is methyl hydroxide, *wood alcohol*. From the reaction just given, it appears probable that this compound is methane in which a hydroxyl group has been substituted for a hydrogen atom. It is an organic hydroxide, and, as might be expected, has basic properties to a certain limited extent. Wood alcohol is commercially obtained by the destructive distillation of wood. It is a colorless liquid of low boiling-point. It is used to a large

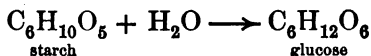
extent as a solvent in the manufacture of varnishes. Wood alcohol is a very convenient fuel where small quantities of heat are required, because it burns with a clean flame of high heat value.

382. Ethyl or Grain Alcohol.—Ethyl hydroxide, C_2H_5OH , *ordinary alcohol*, can be made by heating monochlorethane with potassium hydroxide:

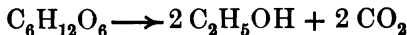


This reaction indicates that ordinary alcohol is a hydroxyl substitution product of ethane. It may also be regarded as an oxidation product of ethane, since the two formulas differ only in the presence of an oxygen atom in the formula of alcohol.

Ordinary alcohol is made in large quantities from grain or potatoes by the process of fermentation. Both of these substances contain a large quantity of starch. This is converted into glucose, a kind of sugar, when heated with dilute sulphuric acid. The sulphuric acid acts merely as a catalytic agent:



After the excess of sulphuric acid has been neutralized with lime, yeast is added, and *fermentation* occurs. Yeast is a microscopic vegetable organism consisting of oval-shaped cells arranged in chains. In solutions which contain suitable food it multiplies rapidly and secretes a substance called *zymase*, which acts as a catalytic agent in converting glucose into alcohol and carbon dioxide:



The alcohol is separated from the resulting solution by repeated distillations. One distillation is not enough to

accomplish the separation, because the boiling-point of alcohol, 78° , is close to that of water. The first portions distilled in each operation are relatively rich in alcohol. By collecting the distillate in fractions, and redistilling these, the separation is made nearly complete. The process is known as fractional distillation. Ordinary commercial alcohol contains from 90% to 95% of the pure substance.

Ethyl alcohol resembles methyl alcohol in its properties. It is a low-boiling liquid, an excellent solvent for organic compounds, and it burns with a clean flame of high heat value. As a constituent of alcoholic beverages it is manufactured in enormous quantities. These owe their intoxicating properties to the presence of alcohol. It is oxidized when taken into the body, furnishing heat.

383. Alcoholic Beverages.—Beer is the product obtained by the fermentation of malt. Barley is placed in a warm moist room until the kernels germinate. When the rootlet has grown to be two-thirds the length of the kernel, the grain is heated to stop the growth. During the germination the starch in the barley is converted into a sugar (maltose). The *malt* thus obtained is ground and boiled with water. Yeast is added to ferment the malt sugar. The fermented liquor is filtered and water added to produce a beer or ale of the desired concentration. Rice and glucose are often used to replace barley. Hops and other flavoring materials are also utilized. Beer contains from 3 to 5 per cent alcohol in addition to soluble materials from the grain.

Wines are produced by the fermentation of fruit juices which contain grape-sugar (glucose). After fermenting, the liquor is allowed to settle and the clear liquid is drawn

off. The wine thus produced, in addition to 15 per cent of alcohol, contains soluble materials derived from the fruit or produced in the fermentation. Whiskey is made by distilling a beer obtained from rye or corn, so that the percentage of alcohol is increased to about 50 per cent. Brandy, resulting from the distillation of wine, may contain 70 per cent alcohol, and rum and gin, derived from fermenting molasses, possess about 75 per cent. All of these distilled liquors contain minute quantities of flavoring materials and traces of acid.

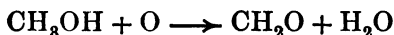
384. Denatured Alcohol.—Denatured alcohol is ethyl alcohol to which wood alcohol or other poisonous substances have been added in order to make its use impossible in beverages and medicines. In countries where a tax is imposed on alcoholic liquors denatured alcohol is often exempt so that the cost of the article in manufacturing operations shall not be prohibitive. Such an exemption law has recently been passed in this country. As a result of it, many kinds of chemical manufactures will be stimulated, and alcohol will probably come into more general use as a fuel.

In the United States methyl alcohol and benzene are the denaturing agents authorized by the Commissioner of Internal Revenue. The proportions by volume are as follows:

- 100 parts ethyl alcohol (not less than 90% strength)
- 10 parts methyl (wood) alcohol
- $\frac{1}{2}$ part benzene

Such alcohol is classed as completely denatured, but there are many formulas for denaturization to suit special purposes.

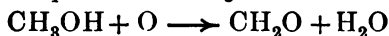
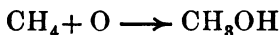
385. Aldehydes. — Another series of compounds, known as aldehydes, are closely related to alcohols. They can be made by an oxidizing process which results in the taking away of two hydrogen atoms from the molecule. Thus *formaldehyde* is made by passing a mixture of methyl alcohol vapor and air over a heated copper spiral or heated asbestos which is sometimes platinized :



Formaldehyde is a very valuable disinfectant and preservative. It is a gas at ordinary temperatures, but it comes into the market as a water solution known as *formalin*.

ORGANIC ACIDS.

386. These may be regarded as oxidation products of the aldehydes. Thus, in oxidizing hydrocarbons, we obtain successively alcohols, aldehydes, and acids :

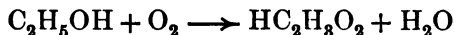


387. Properties. — The organic acids have in a less degree the characteristic properties of the familiar inorganic acids. They neutralize bases, forming salts and water, and they often act directly on metals, liberating hydrogen. Their water solutions do not conduct the electric current very well, and hence they are weak acids.

388. Formic Acid. — Formic acid, CH_2O_2 , or HCHO_2 , is the lowest member of the series; it is of no practical importance. The sting of ants is said to be due to this compound.

389. Acetic Acid and Vinegar. — Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is theoretically derived from the oxidation of ethane, with

the formation of ordinary alcohol and acetaldehyde as intermediate products. Dilute solutions of alcohol, such as are represented in weak wines, or hard cider, when exposed to the air, undergo a fermentation which results in the oxidation of alcohol to acetic acid :

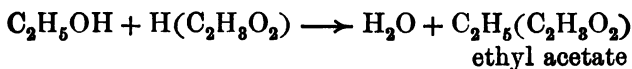
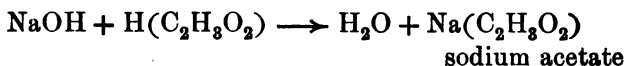


Vinegar is the liquid that results from this action ; it is a dilute solution of acetic acid containing impurities which give it color and modify its flavor. Vinegar is sometimes manufactured by what is called the *quick vinegar process*. Dilute alcohol, to which a certain amount of beer or malt extract has been added, is allowed to trickle over a mass of wood shavings which have been previously treated with vinegar in order to insure the presence of the fermenting organism. The porous mass of shavings makes possible free contact with air, which furnishes the necessary oxygen.

Pure acetic acid is a colorless liquid which freezes on slight cooling. It has a corrosive action on the flesh.

ETHEREAL SALTS, OR ESTERS.

390. Formation and Uses. — Ethereal salts and water are formed by the action of an acid with an alcohol. The reaction is analogous to that which takes place during the formation of a salt by neutralization. The alcohol may therefore be considered as taking the part of a base :



The esters form an important group of compounds. Some are employed in medicine, while others are used in the preparation of perfumery. Many are used in making artificial fruit flavors. The characteristic flavor of the pineapple is due chiefly to ethyl butyrate; oil of winter-green is methyl salicylate.

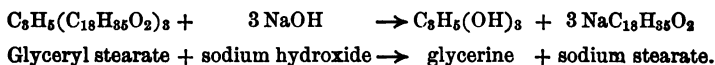
391. Nitroglycerine. — Nitroglycerine, $C_3H_5(NO_3)_3$, is an ester of an alcohol (glycerine) and nitric acid. It is prepared by the action of glycerine, $C_3H_5(OH)_3$, with a mixture of concentrated nitric and sulphuric acids:



The sulphuric acid aids the action by uniting with the water formed during the reaction. The concentration of the free nitric acid is thus kept at maximum. Nitroglycerine is a highly explosive liquid at ordinary temperatures. *Dynamite* is nitroglycerine which has been absorbed by infusorial earth.

392. Oils, Fats, and Soaps. — Oils and fats are esters of glycerine and various fatty acids. The chief constituent of beef tallow is glyceryl stearate, an ester of glycerine and stearic acid, commonly called *stearin*. It is formed by the reaction between one molecule of glycerine and three molecules of stearic acid.

When such a fat is boiled with a solution of sodium hydroxide, a molecule of glycerine and three molecules of sodium stearate, a hard soap, result from the reaction:



Common *hard soap* is a mixture of sodium salts of fatty acids, chiefly stearic, palmitic, and oleic acids. *Soft soap*

is a mixture of the potassium salts of the fatty acids. The term *soap* is applied in general to any metallic salt of a fatty acid.

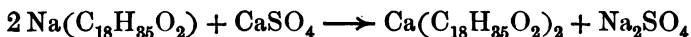
393. Soap-making.—No technical process depends more upon the skill of the operator than the manufacture of soap. In general, soaps may be classed as boiled, semi-boiled, or cold process. Boiled soaps are produced by boiling fats with sodium hydroxide and carbonate. They are often called settled or grain soaps because, during the process of manufacture, the glycerine is separated from the soap. Semi-boiled soaps contain all of the glycerine derived from the fats. Cold process soaps are formed by the direct combination of the fat and alkali, without the aid of external heat.

Most hard soaps used for household purposes are boiled soaps. Soap is made in large iron kettles, fitted with two sets of steam pipes; one a closed coil to supply heat, and the other an open coil to deliver steam through the charge to keep it stirred. Melted fat and about one-fourth the quantity of alkali required for complete saponification are run into the kettle and the steam turned on. The concentration of the alkali is regulated by the kind of fat used. When the mixture has become homogeneous, a more concentrated alkali is added and the boiling continued until a sample shows that the product has the desired consistency. Salt is then added, and the soap being insoluble in brine separates. The kettle is allowed to remain quiet for several hours and the soap collects on top of the liquid. This liquid is called *spent lye*. It contains glycerine, water, salt, and impurities from the alkali and fat. The spent lye is drained off, the salt and glycerine are separated from it, and the layer of soap is boiled with sufficient alkali to

complete the saponification. During this boiling, resin is sometimes added. Pure resin soaps have strong detergent properties, but are too soft and sticky for general use.

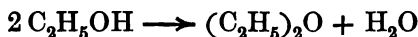
The soap when taken from the kettle is often mixed with one or more of various fillers, such as sodium carbonate, borax, and sodium silicate. Coloring materials and perfumes may also be added. Soaps that float are made light by having air forced through them while they are in the pasty condition. If a good quality of soap is dissolved in alcohol and then dried, a transparent soap is obtained. Sugar and glycerine are often used in the manufacture of transparent soaps. Most soap powders consist essentially of hard soap ground with sodium carbonate.

394. Hard Water and Soap. — When a soluble soap, for example sodium stearate, is used with a water containing calcium ions, an insoluble calcium soap, calcium stearate, is formed:



The soap is said to be destroyed, as good suds cannot be formed until the calcium ions are removed from solution. This explains why hard water is not desirable for washing purposes. The hardness of water is measured by its soap-destroying power. This is commonly due to the presence of calcium and magnesium ions in the water.

395. Ether. — Ordinary ether, $\text{C}_4\text{H}_{10}\text{O}$, may be regarded as ethyl oxide, $(\text{C}_2\text{H}_5)_2\text{O}$. It is prepared by treating alcohol with a dehydrating agent, such as sulphuric or phosphoric acid.



Ether is a volatile, inflammable liquid, boiling at 35° . It is used as a solvent and as an anesthetic.

CARBOHYDRATES.

The carbohydrates are chemical compounds composed of carbon united to hydrogen and oxygen ; the last two elements being in the same proportion as in water.

396. Cellulose. — The cell walls of plants are composed of cellulose, a compound having a percentage composition corresponding to the formula $C_6H_{10}O_5$. Absorbent cotton and the better grades of filter-paper are pure cellulose. It is the chief constituent of straw and wood.

When boiled with acids, cellulose is slowly converted into a sugar called *glucose*. Cellulose dissolves without change in an ammoniacal solution of cupric hydroxide, known as Schweitzer's reagent. The cellulose can be precipitated from such a solution by the addition of hydrochloric acid. Cellulose is dissolved in zinc chloride in making the filaments for incandescent electric light bulbs.

If the formula for cellulose is considered to be $(C_6H_{10}O_5)_n$, from two to six nitro (NO_2) groups can be introduced into the molecule. Thus, when pure cotton fibre is treated with a mixture of nitric and sulphuric acids, products are obtained which may contain two, three, four, five, or six nitro groups ; the number depending upon the concentration of the acids and the time during which they are allowed to act.

The di-, tri-, tetra-, and penta-nitrocelluloses are known as soluble guncotton. Hexanitrocellulose is insoluble guncotton. *Collodion* is a solution of soluble guncotton in a mixture of alcohol and ether. When such a solution is to be used as liquid court plaster, about 5% of Venice turpentine and 3% of castor oil are added to prevent the shrink-

age of the film and to make it more flexible. *Celluloid* is a guncotton incorporated with camphor. *Explosive gelatine* consists of guncotton dissolved in nitroglycerine. *Ballistite* contains equal parts of soluble nitrocellulose and nitroglycerine, to which is added a small quantity of a substance (diphenylamine) to increase its stability. *Cordite* contains nitroglycerine, guncotton, and vaseline. Explosive gelatine is used in blasting; ballistite and cordite are examples of smokeless powders.

397. Paper Making. — Much wood is used in the manufacture of pulp from which paper is made. The wood is finely shredded, then boiled under pressure in a solution of either sodium hydroxide or a mixture of calcium and magnesium bisulphites. The fibre is bleached with chlorine and pressed into sheets called *pulp*. As the fibres of wood are very short, the paper made from wood is not tough.

Better grades of paper are made from cotton and linen rags. The rags are shredded, cleansed in a solution of sodium hydroxide, and bleached with chlorine obtained from bleaching-powder. The excess of chloride of lime is removed by sodium sulphite. Loading material (barium or calcium carbonate) and size (starch or similar material) are added to give stiffness to the fibre and to overcome capillarity.

After the fibre, loading material, and size have been thoroughly mixed in water, the paper is *laid* by shaking it on fine screens. The watery liquid passes through the screen, while the fibre is left matted in a uniform layer. The layer of matted fibre is pressed between felt, dried, and finally calendered by being passed between heated rolls.

Filters and blotting-paper contain neither loading ma-

terial nor size. Newspaper is made from pulp, and may not have been bleached by chlorine. The best paper is made from linen.

398. Starch.—Starch ($C_6H_{10}O_5$)_n is found as granules in the cells of plants. These granules consist of a wall of starch cellulose within which is soluble starch. Starch is insoluble in cold water, but boiling water causes the walls of the starch granules to burst, and the soluble starch enters solution. Much starch is obtained from potatoes and corn.

No matter what the source, the method of preparing starch is the same. The material is crushed, then macerated with water, and the milk-colored liquid filtered through cloth fine enough to prevent all besides the water and starch from passing. The starch is allowed to settle to the bottom of the containing vessel, from which it is afterwards removed and dried.

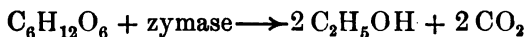
Dilute acids convert starch into glucose, and much starch is used for this purpose. *Dextrine* is prepared by heating dry starch to about 250° C. It is a valuable constituent of food, and is used in making paste similar to that on the back of postage stamps.

Sprouting barley contains an enzyme (ferment) known as *diastase*, which is capable of converting starch into a sugar named *maltose*. In the manufacture of *malt*, the grain is allowed to germinate to produce the enzyme, after which the process is stopped by heating the barley to 60°. At a temperature of about 70° C., the diastase rapidly converts the starch which the grain contains into maltose and dextrose.

399. Sugars.—A very large number of sugars are known. *Fructose*, or fruit sugar; *glucose*, or grape sugar;

and *saccharose*, or cane sugar, are among the more important. Fructose and glucose have the empirical formula $C_6H_{12}O_6$; the formula for saccharose is $C_{12}H_{22}O_{11}$.

Glucose is converted by a ferment (zymase) secreted by the yeast plant into alcohol and carbon dioxide:



This fermentation is made use of in the raising of bread and in the preparation of alcohol. It also is the cause of the formation of hard cider.

The manufacture of glucose from starch has already been referred to. Large quantities of glucose are used in making candies and table syrups. Common sugar, saccharose, is obtained from the sap of the sugar-cane, sugar-beet, and sorghum. It is also the principal constituent of maple sugar.

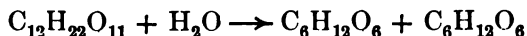
400. Sugar Manufacture and Refining.—Sugar is obtained from sugar-cane or beets by macerating the fibre. Slaked lime is added to the juice to prevent fermentation and precipitate the albuminous substances coming from the plant cells. The solution is then filtered through cloth and evaporated in a vacuum pan at a temperature of about 66° . If the evaporation were carried on under ordinary pressure, the temperature would become sufficiently high to convert the saccharose into a mixture of glucose and fructose.

As soon as a sample taken from the vacuum pan shows that sugar will crystallize when the syrup cools, the solution is removed from the pan and allowed to cool. The crystals are dried in centrifugal machines. The product obtained is usually raw sugar which must be refined before being placed on the market. Nearly all sugar refineries are in the northern states.

The raw sugar is dissolved in large vats and the syrup pumped to the top of high buildings, where it is mixed with lime and a little boneblack to precipitate any albuminous material that may have been left in the sugar. The syrup is then filtered through long sacks, called bag-filters, to remove the coarse impurities that are suspended in the solution. After this, the liquid is filtered through boneblack to remove the coloring-matter. The purified syrup is boiled in vacuum pans as in the case of raw sugar.

Crystals of pure sugar have a pale, yellowish tint. As most people are ignorant of this fact and demand that a white sugar be sold them, the sugar refiners add some blue pigment to the sugar, for example ultramarine. The blue counteracts the yellow and causes the sugar to appear white.

Saccharose is converted into glucose and fructose by boiling:



Dilute acids hasten this action, which is known as inversion. For this reason vinegar is often added to sugar during the making of candy that is to be pulled.

Zymase does not convert saccharose into alcohol and carbon dioxide. However, the yeast plant secretes another ferment called *invertase* which changes saccharose to a mixture of glucose and fructose. These, as has already been mentioned, can be fermented by zymase.

Common sugar melts at 160° C. to a colorless liquid which solidifies on cooling to a transparent amber-colored mass, called *barley sugar*. When sugar is heated to 215° C., some water is expelled and a brown mass, *caramel*, is obtained.

APPENDIX

APPENDIX.

I. PHYSICAL CONSTANTS OF THE IMPORTANT ELEMENTS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHTS.		VALENCE.	SPECIFIC GRAVITY.		MELTING POINT.	BOILING POINT.
		Approximate.	Exact O = 16.		Water = 1.	Air = 1.	° C.	° C.
Aluminum	Al	27	27.1	III	2.6		657	1500-1700
Antimony	Sb	120	120.2	III V	6.6		630	1500-1700
Argon	A	40	39.9	—		1.38	-188	-188
Arsenic	As	75	75.0	III V	5.7		...	<360 volatile
Barium	Ba	137	137.4	II	3.8		850	950
Bismuth	Bi	208	208.0	III V	9.7		269	1435
Boron	B	11	11.0	III	2.6		infusible	3500
Bromine	Br	80	79.96	I	3.1		-7.3	59
Cadmium	Cd	112	112.4	II	8.6		322	778
Calcium	Ca	40	40.1	II	1.5		about 800	...
Carbon	C	12	12.00	IV	1.7-2.1		sublimes	3500
Chlorine	Cl	35.5	35.45	I		2.49	-102	-33.6
Chromium	Cr	52	52.1	II III VI	6.9		1515	...
Cobalt	Co	59	59.0	II	8.7		1530	...
Copper	Cu	63.6	63.6	I II	8.9		1065	2100
Fluorine	F	19	19.0	I		1.31	-223	-187
Gold	Au	197	197.2	I III	19.3		1065	...
Helium	He	4	4.0	—		0.13	-271	-267
Hydrogen	H	1	1.008	I		0.07	-252.5	-252.5
Iodine	I	127	126.97	I	4.9		114	184
Iron	Fe	56	55.9	II III	7.8		1950	...
Lead	Pb	207	206.9	II IV	11.3		327	1400-1600

ELEMENT.	SYMBOL.	ATOMIC WEIGHTS.		VALENCE.	SPECIFIC GRAVITY.		MELTING POINT.	BOILING POINT.
		Approximate.	Exact. O = 16.		Water = 1.	Air = 1.	° C.	° C.
Lithium	Li	7	7.03	I	0.59		186	<1400
Magnesium	Mg	24.3	24.36	II	1.7		632	1100
Manganese	Mn	55	55.0	II IV	7.4		1245	...
Mercury	Hg	200	200.0	I II	13.6		-38.8	357
Nickel	Ni	58.7	58.7	II	8.7		1484	...
Nitrogen	N	14	14.01	III V		0.96	-210	-195
Oxygen	O	16	16.00	II		1.10	<-230	-182
Phosphorus	P	31	31.0	III V	yellow 1.8		yellow 44.2	290
Platinum	Pt	195	194.8	IV	21.5		1710- 1780	...
Potassium	K	39	39.15	I	0.87		62.5	757
Silicon	Si	28	28.4	IV	2.0		...	3500
Silver	Ag	108	107.93	I	10.5		961	2050
Sodium	Na	23	23.05	I	0.97		97.6	877
Strontium	Sr	87	87.6	II	2.5		900	...
Sulphur	S	32	32.06	II IV VI	2.0		rhombic 114.5	444.8
Tin	Sn	119	119.0	II IV	7.3		232	1450- 1600
Zinc	Zn	65	65.4	II	7.1		419	918

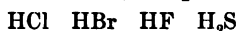
III. GENERAL RULES FOR SOLUBILITY.

Certain generalizations can be made concerning compounds shown in the table on the opposite page. The exceptions to these generalizations are few and unimportant.

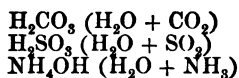
1. All *sodium, potassium, and ammonium* compounds are *soluble* in water.
2. All *nitrates, chlorates, and acetates* are *soluble* in water.
3. All *chlorides* are *soluble*, except those of silver, mercury (mercurous), and lead (lead slightly soluble).
4. All *sulphates* are *soluble*, except those of barium, lead, and calcium (calcium slightly soluble). The silver and the mercurous sulphates are only moderately soluble.
5. All *carbonates* are *insoluble*, except those of sodium, potassium, and ammonium.
6. All *oxides and hydroxides* are *insoluble*, except those of ammonium, sodium, potassium, and barium; calcium hydroxide is slightly soluble.

IV. VOLATILITY OF COMPOUNDS THAT MAY RESULT FROM DOUBLE DECOMPOSITIONS.

1. Compounds volatile at ordinary temperatures:



2. Compounds decomposing at ordinary temperatures yielding volatile products:



3. Compounds volatile at varying temperatures below 338° (boiling-point of sulphuric acid):

	BOILING-POINT.		BOILING-POINT.
H ₂ O,	100°	HNO ₃ ,	86°
HCl (aqueous solution),	110°	HNO ₃ (aqueous solution),	120°
HBr (aqueous solution),	126°	HC ₂ H ₃ O ₂ ,	118°

V. WEIGHT OF ONE LITER OF COMMON GASES UNDER STANDARD CONDITIONS.

Acetylene,	1.162 grams	Hydrogen sulphide,	1.523 grams
Ammonia,	0.762 "	Marsh gas,	0.716 "
Carbon dioxide,	1.965 "	Nitrogen,	1.254 "
Carbon monoxide,	1.250 "	Nitric oxide,	1.340 "
Chlorine,	3.166 "	Nitrous oxide,	1.968 "
Hydrogen chloride,	1.628 "	Oxygen,	1.429 "
Hydrogen,	0.0898 "	Sulphur dioxide,	2.861 "

VI. PRESSURE OF WATER VAPOR, OR AQUEOUS TENSION.

(In millimeters of mercury.)

TEMPERATURE.	PRESSURE.	TEMPERATURE.	PRESSURE.
0.0° C.	4.6 mm.	21.5° C.	19.1 mm.
5	6.5	22	19.7
10	9.2	22.5	20.3
10.5	9.5	23	20.9
11	9.8	23.5	21.5
11.5	10.1	24	22.1
12	10.5	24.5	22.8
12.5	10.8	25	23.5
13	11.2	25.5	24.2
13.5	11.5	26	25.0
14	11.9	26.5	25.7
14.5	12.3	27	26.5
15	12.7	27.5	27.3
15.5	13.1	28	28.1
16	13.5	28.5	28.9
16.5	14.0	29	29.8
17	14.4	29.5	30.7
17.5	14.9	30	31.6
18	15.4	40	54.9
18.5	15.9	50	92.1
19	16.4	60	149.2
19.5	16.9	70	233.8
20	17.4	80	355.4
20.5	17.9	90	526.0
21	18.5	100	760.0

VII. THE KINETIC THEORY OF GASES.

The physical structure made evident in the uniform behavior of gases, under changes of temperature and pressure, is explained by a simple mechanical conception, the kinetic theory of gases.

According to this hypothesis a gas consists of many minute particles, exerting practically no attraction for one another, but moving freely with great velocity. If we consider a cube to contain a number of such particles, moving in all directions, it is evident that they must collide among themselves and against the walls of the vessel, in either case rebounding and continuing their motion in the new direction until the next collision.

This continual bombardment exerts a force (pressure) against the walls, which must depend upon the number of blows, the mass and the speed of the particles. If, now, the particles (molecules) in our cube were confined to the lower half, the number of blows against the surface would be doubled, and the mass and speed being the same, the pressure would be doubled. That is, the pressure would vary inversely as the volume.

Let us express this relation mathematically. If m is the mass of the molecule, n the number of molecules, v their speed, l the edge of the cube, a molecule would strike the wall $\frac{v}{l}$ times a second. At each collision its momentum would be changed $2mv$, so that the *total* force exerted on the surface of the cube by n molecules would be $n \cdot 2mv \cdot \frac{v}{l}$ or $\frac{2mnv^2}{l}$. As the cube has six faces, the total surface of the cube is $6l^2$. The force per unit area, or pressure (P),

would be $\frac{2mnv^2}{l} + 6P$ or $\frac{2mnv^2}{6l^3}$. As l^3 is the volume (V),

$$P = \frac{mnv^2}{3V}, \quad (1)$$

$$\text{or } PV = \frac{mnv^2}{3} = \text{a constant.} \quad (2)$$

If the number, mass, and speed of the molecules do not change, the expression $\frac{mnv^2}{3}$ is a constant. Hence the product of the pressure and volume of a gas at a given temperature is a constant. This is Boyle's law.

Heat is defined as molecular motion. The speed of the molecules determines the temperature. If the speed of the particles in the cube increases, it is evident that the number of blows will increase; that is, the volume of the gas remaining constant, the pressure increases with the temperature. In equation (2) $PV = \frac{mnv^2}{3}$, if v varies, V

or P (or both) must vary. That is, if the *pressure* remain constant, the volume of the gas will vary as the temperature (Charles' law). If the *volume* of the gas remains constant, the pressure will vary as the temperature.

Two masses have the same temperature when they do not impart energy to each other. Two molecules, then, at the same temperature, must have equal kinetic energy, otherwise they would be hastened or retarded on collision.

$$\frac{1}{2}mv^2 = \frac{1}{2}m'v'^2. \quad (3)$$

From (1) it follows that two gases would have equal pressures when

$$\frac{nmv^2}{3V} = \frac{n'm'v'^2}{3V'}. \quad (4)$$

If the temperatures are equal, it follows from (3) that

$$mv^2 = m'v'^2. \quad (5)$$

Eliminating the equal factors from both members of (4) we have

$$\frac{n}{V} = \frac{n'}{V'}. \quad (6)$$

If the volumes are equal, $V = V'$, hence $n = n'$. That is, equal volumes of gases under similar conditions of temperature and pressure, contain equal numbers of molecules. This is Avogadro's hypothesis.

These equations give the explanation of other physical phenomena. Thus, from (4) we get

$$v : v' :: \sqrt{\frac{mn}{V}} : \sqrt{\frac{m'n'}{V'}}, \quad (7)$$

mn being the total mass of the gas; $\frac{mn}{V}$ is the density; hence the velocity varies inversely as the square root of the density. (Law of diffusion.)

We can also find the absolute speed. From (1):

$$v = \sqrt{\frac{3PV}{mn}}. \quad (8)$$

One liter of oxygen (V) weighs 1.428 grams (mn) under standard conditions. Standard pressure of 76 cm. of mercury is equivalent to about 1000000 dynes per square centimeter. Substituting these values,

$$v = \sqrt{\frac{3 \times 1000000 \times 1000}{1.4}},$$

we find the speed per second to be about 46000 cm. (over a quarter of a mile), or about as fast as a rifle bullet. Hydrogen, in accordance with (7), should move four times as fast.

These equations do not take into consideration the size of the molecules or the actual space they occupy. A study of gases under high pressure shows that the diameter of the hydrogen molecule is less than one ten-millionth of a centimeter, and that the molecules occupy about one thousandth of the volume.

In the case of liquids, the molecules have considerable freedom of motion, as is evident in the diffusion of liquids. The molecules are probably closer together than in gases, thus resisting pressure, and their mutual attraction is sufficient to prevent their rapid separation. When a solid is dissolved in a liquid, it acts physically very much as if it were a gas occupying the volume of the solvent.

In solids the motion is much more circumscribed and the molecules are still closer together. Diffusion and evaporation are less in the case of solids than in liquids. The application of conceptions derived from the kinetic theory gives one mathematical expression applicable to solids:

Specific heat \times atomic weight = 6.3 (approximately),
which is Du Long and Petit's law.

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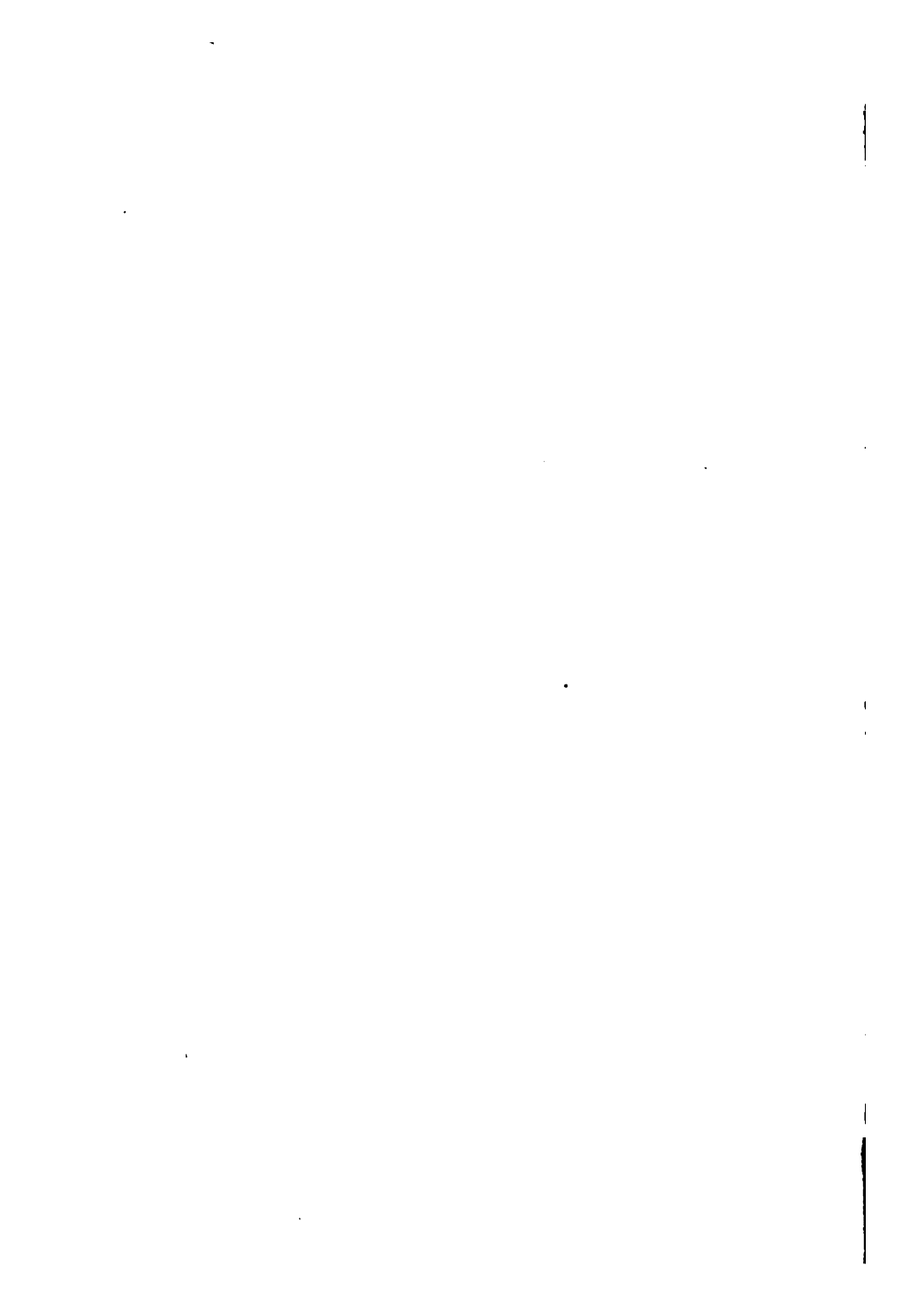
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